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New data on the slag-minerals nagelschmidtite and steadite.

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NAGELSCHMIDTITE.

IN 1937 G. Nagelschmidt described a new silicophosphate mineral obtained from basic slag. It resembled the earlier described silico-carnotite (A. Carnot and A. Richard, 1883; D. P. Riley and E. R. Segnit, 1949) in its solubility in citric acid. Nagelschmidt gave optical, chemical, and X-ray data which indicated that the material had a composition of approximately $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$, and agreed closely with a phase reported by G. Trömel (1943) in his investigation of the system $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$. The material was further considered by M. A. Bredig (1941), who published cell dimensions worked out from powder photographs, assuming that nagelschmidtite was a solid solution of tricalcium phosphate in a predicted high-temperature hexagonal form of dicalcium silicate. R. L. Barrett and W. J. McCaughey (1942) gave further data, chiefly connected with phase relationships in the binary system $\text{Ca}_2\text{SiO}_4-\text{Ca}_3\text{P}_2\text{O}_8$. Finally, S. O. Agrell (1946) published further data on the slag mineral, giving the chemical analyses and optical properties of two samples, together with a discussion of the phase relationships of the material in slags, and hence in the binary system mentioned above. The name 'nagelschmidtite' is due to Barrett and McCaughey.

Description of samples.

During this examination at least two varieties of colourless silicophosphate were encountered. One of these is dull and cloudy, sometimes almost opaque; the second is quite clear and transparent. These will be

referred to generally as the 'cloudy phase' and the 'clear phase' respectively. In one case (slag C, below) the clear phase itself is often divided into an inner and outer zone of crystallographically dissimilar material.

A. A fine-grained slag (specimen 47715, Dept. Min. Petr.), composed of the clear phase and iron oxide, with minute needles of apatite in occasional vugs. The silicophosphate makes up about 70 % of the slag. It has a good cleavage, and shows no more than a slight tendency to elongation parallel to this cleavage, which is basal. A small amount of the cloudy phase occurs around the edge of some crystals. It is generally associated with the oxide phase. The latter is a wüstite, which, with some calcium ferrite, makes up the rest of the slag.

B. A slightly coarser slag (54216) with a lower percentage of phosphorus. Small vugs contain needles of apatite or steadite, and minute colourless hexagonal plates of tricalcium silicate. This slag together with the following analysis, was supplied by Mr. J. H. Whitely of the Consett Iron Co. Ltd., Durham: SiO_2 15.60, Fe 10.00, MnO 5.58, CaO 46.60, MgO 9.02, S 0.33, P_2O_5 6.24. It contains considerable free iron. The chief constituent is the cloudy phase; the clear phase is entirely absent. This material shows irregular extinction between crossed nicols. The grain-size is of the order of 0.2 mm. Orange coloured magnesiowüstite and occasional crystals of apatite make up the remainder of the slag.

C. This slag (57554) contains both the cloudy and the clear phases of the silicophosphate material. The former always occurs as a rim or outer zone around the latter. The rimming is rather indistinct in ordinary light but quite sharp when seen between crossed nicols (figs. 1-3). The cloudy material stands out by virtue of its higher birefringence. The inner clear zone of this slag shows phenomena which are not seen, at least as clearly, in any of the other slags of the group examined. It appears quite homogeneous in ordinary light, but between crossed nicols two zones with a sharply defined border between them can be seen. The inner of these two clear zones has a lower birefringence, and extinguishes homogeneously. The outer zone shows variable extinction possibly due to composition zoning of the crystals. Apart from the birefringence and the extinction there is no sensible difference in the optical properties. The oxide phase is dark-red magnesiowüstite. It is interstitial and evidently a late crystallization. A little calcium ferrite is also present.

D (57555). Composed almost entirely of the cloudy phase with interstitial wüstite. The material causing the cloudiness is much coarser in this sample and can be resolved into tiny droplets arranged in parallel fashion.

E. Sections cut from this slag (57556, from Messrs. Stewart and Lloyd of Corby) show considerable variation. One side of the hand-specimen



FIG. 1. Crystal of the phosphate phase in a basic open-hearth slag. Plane polarized light.



FIG. 2. As fig. 1, showing zoning between crossed nicols.

is rather porous and was more quickly cooled than the other side, except for a glazed edge where the still molten slag had flowed away. Sections of the porous part consist chiefly of rounded grains of the clear phase which are entirely free from the cloudy phase and are sensibly uniaxial. Sporadically distributed are small patches of cloudy material which increase in size and number as one approaches the other side of the specimen. Rimming is not characteristic; rather, a grain is completely or only half cloudy. The dividing line between crossed nicols is still quite sharp. The cloudy phase nearly always occurs associated with the oxide phase, which is interstitial and present in only small amount.



FIG. 3. Sketch of fig. 1. Clear zone, nagelschmidtite; dark stippling, larnite at extinction; light stippling, larnite; shaded area, chiefly wüstite.

F (57557). A thin section only, from a group of slags containing only 1-2 % P_2O_5 . This section is of interest because it contains almost

identical rimming phenomena as in sample C, and yet it contains little phosphorus.

Numerous other samples were also examined, but did not differ appreciably from one or other of those described above.

Chemical composition.

Samples of the clear and the cloudy phases were separated from specimens A and B respectively by the usual methods of centrifuging in heavy liquids. The powders eventually obtained for analysis still contained a small amount of magnesiowüstite as inclusions too small to separate. The results of the chemical analyses are given in table I, columns 2 and 3, together with analyses published by other authors, and the theoretical composition for $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$.

The low summation of all but one of the analyses seems to have been due to the absorption of iodoform (from the decomposition of the methylene iodide used in their separation) by the very fine powders used. Nagelschmidt's powders were rather fine, as were also those of Agrell. The latter states that (private communication) his powders on heating gave off iodine vapours. The powder used for analysis 2 also gave off iodine vapours when heated in a closed tube, and a yellow sublimate, evidently iodoform, condensed on the cool part of the tube. The same powder had a loss on ignition of about 3.5 %. The powder of analysis 3 was coarser.

TABLE I. Chemical analyses of nagelschmidtite.

		1.	2.	3.	4.	5.	6.	7.
SiO ₂	. .	18.35	19.51	18.85	20.92	19.96	17.7	17.9
P ₂ O ₅	. .	21.69	16.80	5.60	12.28	13.10	20.0	19.9
CaO	. .	59.96	55.62	62.88	57.64	58.70	58.4	58.3
MgO	. .	—	0.04	1.21	0.92	0.87	0.6	—
FeO	. .	—	—	2.77	—	—	—	—
MnO	. .	—	1.24	—	0.41	0.67	—	—
Al ₂ O ₃	. .	—	—	5.00	1.52	0.80	0.4	—
Fe ₂ O ₃	. .	—	2.73	3.73	1.61	2.03		
TiO ₂	. .	—	—	—	0.43	1.00	—	—
CO ₂	. .	—	—	—	0.48	nil	—	—
H ₂ O	. .	—	—	—	0.87	nil	—	—
		100.00	95.94	100.04	97.08	97.13	97.1	96.1

1, Theoretical composition for $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$. 2, Sample A (clear phase), also loss on ignition 3.5 %, this paper. 3, Sample B (cloudy phase), this paper. 4 and 5, Agrell, 1946. 6 and 7, Nagelschmidt, 1937; two analyses of the same material.

The six analyses show considerable variation, which is to be expected from any of the published diagrams representing the phase relations of

the system $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$. All show extensive solid solution around this composition.

Barrett and McCaughey give a useful general formula for compositions lying in this system— $\text{Ca}_{(2\text{Si} + \frac{3}{2}\text{P})}(\text{P}, \text{Si})_{12}\text{O}_{48}$. In table II the analyses have been worked out on this basis. The final column gives the figure for calcium (worked out from the ratio $2\text{Si} + \frac{3}{2}\text{P}$) which would be needed in each case to bring the analysis exactly into the system. In the new analyses the iron and magnesia are known to be present as impurities.

These compounds, as was pointed out by Nagelschmidt, are quite readily soluble in organic acids. Their phosphorus content is therefore directly available to plants when the ground slag is used as a fertilizer.

TABLE II. Formulae on the basis of 48 oxygen atoms.

Analysis no.					Theoretical Ca.
2.	(Ca, Mn) _{21.4}	P _{5.0}	Si _{6.9}	O ₄₈	Ca _{21.4}
3.	Ca _{24.2}	P _{1.7}	(Si, Al) _{9.9}	O ₄₈	Ca _{22.4}
4.	(Ca, Mg, Mn, Fe) _{22.7}	P _{3.6}	(Si, Ti, Al) _{8.2}	O ₄₈	Ca _{21.8}
5.	(Ca, Mg, Mn, Fe) _{23.4}	P _{3.8}	(Si, Ti, Al) _{7.5}	O ₄₈	Ca _{21.6}
6 and 7.	Ca _{18.4}	P _{5.0}	Si _{5.2}	O ₄₈	Ca _{17.9}

From table II it can be seen that in each case the composition falls close to the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ system.

Optical properties.

The clear phase.—The material of sample A is characteristic. It is quite colourless and biaxial positive with a very small optic axial angle. The maximum and minimum refractive indices observed in sodium-light were 1.668 and 1.660 (± 0.002). A good cleavage is frequently seen; it is parallel to the fast vibration direction in the grains, and is evidently basal. A second possible cleavage is sometimes seen at right angles to the first. Crystal edges are not often seen, but occasional nearly isotropic basal sections giving a centred almost uniaxial interference figure have hexagonal outlines. The evidence here seems to confirm Bredig's work on the hexagonal nature of nagelschmidtite.

Of considerable interest is the zoning of the clear phase in sample C. As mentioned above, there is very little difference between the optical properties of the two parts, but the division between the two zones is very distinct when seen between crossed nicols. Little positive proof of the relative natures of these two zones can be obtained; it is thought, however, that the difference is purely structural. The part with the irregular extinction is probably a lower-temperature form. This is discussed in more detail below.

The cloudy phase.—Sample B is characteristic of this type. It is colourless, but always turbid. It is biaxial positive, with a moderate to low optic axial angle. The maximum and minimum refractive indices observed in sodium-light were 1.675 and 1.661. The birefringence is much higher than that of the clear phase. The grains show no crystal form, and rarely cleavage. Extinction is irregular.

The optical properties of these phases are set out in table III, together with the optics of the other analysed samples of table I. Agrell (1946) and K. Balajiva and co-authors (1946) have also given a number of refractive index determinations which show a continuous increase as silicon replaces phosphorus.

TABLE III. Optical data of nagelschmidtite.

Analysis no.	Refractive indices.		Bire- fringence.	2V(+).	Variety.
	Max.	Min.			
2.	1.668	1.660	0.008	Very small	Clear
3.	1.675	1.661	0.014	Moderate to small	Cloudy
4.	1.690	1.680	0.010	10°	Clear
5.	1.693	1.682	0.011	10°	Clear
6 and 7.	1.661	1.652	0.009	Small	Clear

The nature of the two phases.

The clear phase.—The X-ray powder diagram proves this to be similar to the mineral examined by Nagelschmidt. Table IV gives the spacings and relative intensities of the strongest lines of the material extracted from sample A, and the corresponding lines of Nagelschmidt's material from his paper.

TABLE IV. X-ray spacings and intensities of nagelschmidtite.

1.		2.	
<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>
3.80	m	3.93	w
3.42	m	3.54	w
2.80	s	2.85	s
2.66	vs	2.70	s
2.20	m	2.22	vw
1.94	s	1.960	s
1.54	w	1.562	w
1.48	w	1.485	m
1.34	m	1.346	m

1, Sample A, this paper. 2, Nagelschmidt, 1937.

The small differences between the two samples are always in the same direction, and are to be ascribed to the difference in com-

position (analyses 2 and 6, table I). This, then, is the phase which Bredig (1943) correlates with a high-temperature hexagonal form of dicalcium silicate solid solution, and which has been termed 'nagelschmidtite'.

The cloudy phase.—An X-ray powder photograph of the material separated from slag sample B is reproduced in fig. 4 together with photographs of larnite from Scawt Hill, Co. Antrim, and nagelschmidtite from

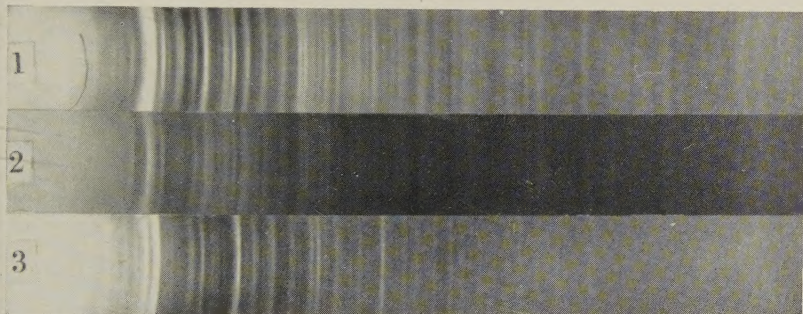


FIG. 4. X-ray powder photographs of: (1) larnite from Scawt Hill, Co. Antrim; (2) larnite solid solution from slag B; (3) nagelschmidtite from slag A.

sample A. By a comparison of the photographs it can be seen that the cloudy phase is not the same as nagelschmidtite, but in fact, is related to larnite, the β -form of dicalcium silicate. The cloudiness is due to the fact that it cannot take as much material into solid solution as the higher-temperature form. In slag sample D the material causing the cloudiness is much coarser than usual. A regular arrangement of small globules is seen under the high power. This is very reminiscent of the exsolved material obtained by the writer on the slow cooling of artificial melts of silicate compounds beyond their solid solution limits.

A noteworthy feature of the larnite solid solution in these occurrences is the lack of the fine multiple twinning which is usually associated with this phase of dicalcium silicate. The usual interpretation of the twinning is that it has been formed during inversion from a higher-temperature form. The optical data of a typical larnite are α 1.707, β 1.715, γ 1.730, 2V positive, moderate to small (C. E. Tilley, 1929). Lower refractive indices of the slag material are caused by phosphorus in solid solution. It is thought that probably all the cloudy phase in these slags is larnite solid solution. Only the extra zone in slag C can be tentatively classed as the α' -form, bredigite.

The system dicalcium silicate-tricalcium phosphate with special reference to slags.

All of the colourless silicophosphate phases in these slags are considered to be forms of dicalcium silicate. For convenience, the names of the slag and natural mineral forms will be used. The clear phase will be called nagelschmidtite (hexagonal α - Ca_2SiO_4) and the cloudy phase larnite (β - Ca_2SiO_4) with, here, some $\text{Ca}_3\text{P}_2\text{O}_8$ in solid solution). Bredigite (orthorhombic α' - Ca_2SiO_4) (C. E. Tilley and H. C. G. Vincent, 1948) may occur in slag C. The various forms of pure Ca_2SiO_4 are summarized in table V.

TABLE V. Properties of the four forms of dicalcium silicate, Ca_2SiO_4 .

Form.	Name.	Crystal system.	Inversion to higher form.	α .	Optical data.			2V(+).
					β .	γ .		
α	—	Hexagonal	—	—	—	—	—	—
α'	Bredigite	Orthorhombic	1450° C.	1.712	1.716	1.725	30°	
β	Larnite	Monoclinic	675° C.	1.707	1.715	1.730	—	
γ	—	Orthorhombic	850° C.	1.642	1.645	1.654	60°	

The order of inversion of the forms on cooling is $\alpha \rightarrow \alpha' \rightarrow \beta \rightarrow \gamma$, and on heating $\gamma \rightarrow \alpha' \rightarrow \alpha$. If the β -form is stabilized, the order of inversion on heating is $\beta \rightarrow \alpha' \rightarrow \alpha$ (G. Trömel, 1949). J. H. Welch and R. W. Nurse (private communication) have confirmed these inversion temperatures by means of thermal analysis.

The phase relationships of silicocarnotite.—This compound undergoes a change in the solid state. In order to gain some idea of the temperature of this change, a number of samples of silicocarnotite were heated to various temperatures up to 1450° C. These results indicated that a reversible change took place between 1400° C. and 1450° C. (D. P. Riley and E. R. Segnit, 1949). A synthetic product of this composition prepared at 1500° C. gave, however, a nagelschmidtite powder photograph (R. Klement and F. Steckenreiter, 1940). Silicocarnotite evidently exists in a high-temperature hexagonal form analogous to nagelschmidtite, and, under certain conditions, metastable (see also K. Balajiva and co-authors, 1946). The silicocarnotite of slags crystallizes below the inversion temperature.

In the simple binary system as suggested by M. A. Bredig in 1943 (see fig. 5), a nagelschmidtite would crystallize from a melt of the composition $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ and would invert at a lower temperature to silicocarnotite. When, say, 20 % of iron oxide is present as in a slag, the liquidus temperatures will be lowered to below the inversion tempera-

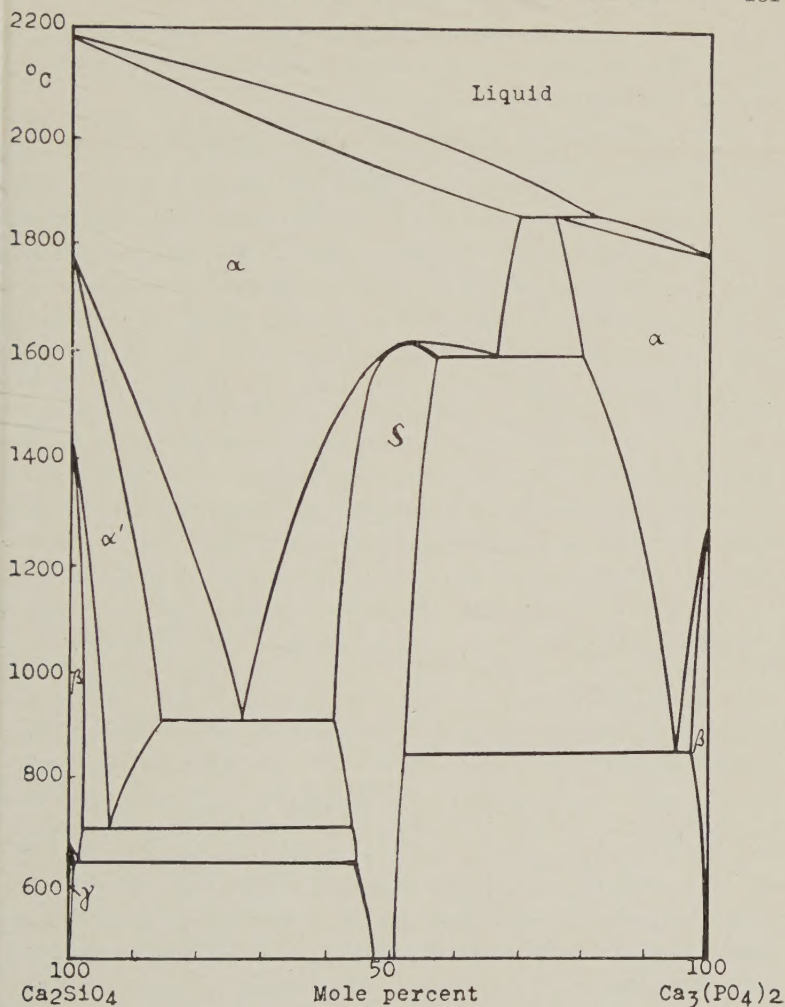


FIG. 5. Phase diagram of the system Ca_2SiO_4 - $\text{Ca}_3\text{P}_2\text{O}_8$ (after Bredig, 1943).

ture, and silicocarnotite will crystallize directly. With a slightly greater silica content, nagelschmidtite and silicocarnotite should occur together. One slag actually showed this association. The dominant phase is nagelschmidtite rimmed by larnite, with silicocarnotite as a subordinate interstitial phase.

The phase relationships of nagelschmidtite.—If all the colourless phases in slags were not dicalcium silicate solid solutions, the latter compound

should be frequently seen rimmed by or associated with nagelschmidtite as a second, ternary, phase. Such an association has not been seen, and is not believed to exist.

Both the nagelschmidtite and larnite phases have been seen in slags ranging in P_2O_5 content from less than 2 % to about 14 %. This represents a range of about 3 % to 20 % P_2O_5 in the silicophosphate material. The rimming is always present to a slight extent in the dominantly nagelschmidtite slags, although pronounced examples of this effect do not seem to be as common as the two extremes. The presence of more than one form of Ca_2SiO_4 in the same slag is due to the stabilizing effect on the higher-temperature forms of material in solid solution (K. T. Greene, 1944).

Crystallization courses in slags will depend to a large extent on the range of temperature of crystallization, which will in turn depend chiefly on the amount of oxide phase present, and to a smaller extent on the P_2O_5 - SiO_2 ratio. During crystallization in these slags, the inversion temperature of nagelschmidtite is passed, and a lower-temperature form begins to crystallize around it (figs. 1-3). In most cases this is larnite. This does not agree well with the latest determinations of the stability range of larnite, which should appear at about 700° C. Unfortunately, there is nothing known about the effect of the phosphorus in solid solution on this inversion temperature. In some slags, however, a third zone between nagelschmidtite and larnite appears (C, p. 174). It is very closely related to the centre zone of nagelschmidtite, but is sharply separated when seen between crossed nicols, has a slightly higher birefringence, and uneven extinction. If the stability order of the four forms of dicalcium silicate is accepted (table V) then it seems sound to assume that we have here a zone of bredigite. The optical properties as far as can be determined agree with those for a bredigite with material in solid solution. Such material should have similar properties to nagelschmidtite. This zone may be more common than has been noticed, but too narrow to be easily seen.

Slags containing only nagelschmidtite will have crystallized above the temperature of phase transition of this form. It is 1450° C. for pure Ca_2SiO_4 ; to what extent this is altered by solid solution is not known, but it is probably lowered somewhat. Below this temperature larnite will crystallize. Nagelschmidtite might therefore be expected in the higher melting-point, and larnite in the lower melting-point slags. In the slags examined, this seemed to be the case, as larnite became commoner with increase in the iron oxide content of the slag.

G. Trömel (1943) showed that the rate of cooling can have a marked

effect on the final mineral composition of the slag. Some of the effects of varying rates of cooling were given by a slag specimen with a glazed surface formed by still liquid slag flowing away from a partially crystallized slag ball. A section cut through the glazed surface was chiefly opaque material with rounded crystals of nagelschmidtite, while the interior, more slowly cooled part of the specimen, was chiefly larnite. The other side of the specimen had undergone fairly rapid cooling, leaving the two phases together. Rimming was not characteristic. The larnite usually started from a grain of wüstite, and worked outwards through perfectly clear nagelschmidtite grains, large areas of which are quite unchanged. The border between the two phases is again sharply defined. The change in this slag seems to be due to inversion which seems to have started mainly from the neighbourhood of wüstite grains in the late crystallizing part of the slag.

The various relationships exhibited by these dicalcium silicate solid solutions in slags cannot be summarized easily. However, those most commonly seen may be stated as follows. If crystallization takes place:

1. Above the α inversion temperature—nagelschmidtite.
2. Below the α inversion temperature—larnite.
3. Passing through the α inversion temperature—nagelschmidtite rimmed by larnite.

The final mineral composition of the slag will therefore depend on its crystallization range, which will in turn depend on the amount of iron oxide present, and on the content of P_2O_5 .

In Bredig's phase diagram (fig. 5) all the boundaries between the Ca_2SiO_4 phases are below the solidus. Some of the inversion temperatures are too high; nevertheless, in slags, the liquidus-solidus boundaries cut across some of the phase boundaries so that nagelschmidtite may frequently crystallize first, to be followed by a lower-temperature form when the requisite temperature is reached. In low-phosphate slags primary crystallization of a lower-temperature form is to be expected.

Finally, it may be emphasized that these investigations were carried out on slags essentially free from fluorine. In the presence of fluorine the crystallization of apatite will shift the equilibrium towards the lime-silica side of the $CaO-SiO_2-P_2O_5$ system.

Note on the occurrence of tricalcium silicate.

In the larnite slag (sample B, p. 174) are occasional vugs into which are growing small crystals. The bulk of these are hexagonal needles of

apatite, but a few minute flat plates with an hexagonal outline sometimes occur. These are sometimes quite transparent, sometimes filled with inclusions. Microchemical tests showed the presence of silica, lime, and phosphorus, and the crystals were decomposed by dilute acetic acid. A Laue photograph showed trigonal symmetry, and the spacings of the main lines of a powder photograph agreed with those given for tricalcium silicate by L. T. Brownmiller and R. H. Bogue (1930).

The interest of this occurrence lies in the fact that the crystals contain considerable phosphorus in solid solution, and that they only occur in the vugs of the slag. No tricalcium silicate was seen in the thin section of the slag.

STEADITE.

V. A. Kroll (1911) applied the term 'steadite' to the small yellowish hexagonal needle-shaped crystals from slag described by J. E. Stead and C. H. Ridsdale (1887). Similar material was also described by G. Hilgenstock (1883) who, like the other authors, assumed that the crystals were a form of tetracalcium phosphate. H. Bücking and G. Linck (1887) also described these crystals, but recognized their similarity to the natural mineral apatite, as did Kroll (1911) later.

Steadite occurs more or less commonly in basic slags. No strict dividing line can be drawn between it and apatite and they both occur under very similar circumstances. It was noticed by earlier workers that steadite was very commonly associated with silicocarnotite. This may be a reflection of the siliceous environment. Steadite is frequently a late constituent to crystallize; its crystals are the commonest in the vugs of basic slags.

Source and description of the samples.

There is little difference in the appearance of steadite from different slags or places. The only outward difference is in colour.

Sample A. Small colourless crystals in vugs in a slag from Irlam, Lancashire (Dept. Min. Petr. no. 57558). The main part of the slag is composed of a dicalcium silicate solid solution, probably larnite, together with wüstite and about 10–15 % of idiomorphic steadite.

Sample B. Abundant, some quite large brownish crystals obtained from the interior of a slag ball from Corby, Northamptonshire (57559). The majority of the crystals are packed with fine inclusions of iron oxide, although the smallest of the crystals are often quite clear.

Sample C. Crystals and grains in silicocarnotite slags from various sources. These are all very similar, and were only examined in thin

section or as minute grains of no crystal shape. They are pale brown in thin section.

Chemical composition.

Two small samples were separated from A and B. Neither sample was perfectly satisfactory owing to the small amounts available and the difficulty of separating the material in the pure state. The results of the analyses are in table VI, together with analyses taken from earlier papers. The new analyses are not perfectly satisfactory, but they do show the essential composition and the presence of considerable amounts of fluorine and silica.

The separation of sample A caused some difficulty because of the presence of large amounts of dicalcium silicate solid solution. When crushed, few grains were entirely free of iron oxide, so that it was not possible to effect a direct gravity separation of the light phases. A separation was eventually made by digesting the powdered slag for some time in dilute acetic acid. This treatment decomposed the dicalcium silicate to a large extent; any remaining grains had a skin of silica which lowered the density enough for a gravity separation to be effective. Any gelatinous silica remaining on the steadite grains was removed by digesting in sodium carbonate solution. Microscopic examination now showed that the grains were quite free from adhering silica, although they still contained inclusions of iron oxide.

TABLE VI. Chemical analyses of steadite.

	1.	2.	3.	4.	5.	6.
P ₂ O ₅ . .	34.19	32.96	33.71	36.77	34.94	42.28
SiO ₂ . .	6.69	6.09	3.90	3.81	3.24	—
CaO . .	52.32	50.87	53.54	53.51	57.55	55.55
Fe ₂ O ₃ . .	—	—	4.86	1.78	—	—
Al ₂ O ₃ . .	—	—	—	1.09	—	—
MnO . .	—	—	0.79	—	—	—
FeO . .	2.87*	8.74*	1.27	2.22	4.00	—
MgO . .	0.35	—	0.49	0.40	—	—
Cr ₂ O ₃ . .	—	—	trace	—	—	—
VO . .	—	—	1.34	—	—	—
S . .	—	—	0.46	trace	—	—
F . .	2.31	3.00	—	—	—	3.76
Less O for F	1.00	1.26	—	—	—	1.59
Total . .	97.73	100.40	100.36	99.58	99.73	100.00

* Total iron as FeO.

1, Sample A, this paper. 2, Sample B, this paper. 3, Stead and Ridsdale, 1887.
4, Bücking and Linck, 1887. 5, Hilgenstock, 1883. 6, Theoretical for 3Ca₃P₂O₈.CaF₂.

Sample B was obtained as individual crystals from the centre of a slag ball. They were almost free of contaminating silicophosphates of other kinds, but contained much included fine iron oxide. The large amount of iron oxide in the analysis can thus be taken as impurity, as qualitative tests on small crystals free from inclusions gave a negative result for iron. The small amount of silicocarnotite present was removed with acetic acid, and any remaining silica with sodium carbonate solution.

The actual silica figures obtained by the usual method of determination in analyses I and II were 4.87 % and 3.76 % respectively. The figures in the table were arrived at by adding the amount of silica theoretically lost with the fluorine during the evaporation with hydrochloric acid. The fluorine determinations are probably a little low, especially in the first case. Only a small amount of material was available, with the result that only a very small volume of thorium nitrate was used for titration. These two analyses have been recalculated on the basis of an apatite formula in table VII with silicon replacing part of the phosphorus. It appears from this table that the fluorine determinations are low, but, with this in mind, the relationship to the apatite structure is evident.

TABLE VII. Analyses I and II calculated to atomic ratios on the basis of the apatite formula $3\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaF}_2$.

I.					Oxide %.	Mol. ratios.	Atomic ratios.	
P ₂ O ₅	.	.	.	.	34.19	0.241	1.64	
SiO ₂	.	.	.	.	6.69	0.111	0.38	
CaO	.	.	.	.	52.32	0.874	2.98	
FeO	.	.	.	.	2.87			
MgO	.	.	.	.	0.35	present as impurity		
F	.	.	.	.	2.31			
					CaF ₂ 4.74%			
Molecular ratio Ca ₃ P ₂ O ₈ :CaF ₂ = 4:1.								

II.						
P ₂ O ₅	.	.	.	.	32.96	0.234
SiO ₂	.	.	.	.	6.09	0.101
CaO	.	.	.	.	50.87	$\left\{ \begin{array}{l} 46.45 \\ 4.42^* \end{array} \right.$
FeO	.	.	.	.	8.74	
F	.	.	.	.	3.00	CaF ₂ 6.15 %
Molecular ratio Ca ₃ P ₂ O ₈ :CaF ₂ =3.4:1.						

* CaO required for fluorine.

D. McConnell (1937) has shown that there can occur a complete substitution of silica and/or sulphur for the phosphorus in the apatite

structure. He was able to show the relationships between ellestadite, which has an apatite structure although it contains very little phosphorus; wilkeite, in which there is a partial replacement of the phosphorus; and apatite. The structures were the same, and there was a continuous change in optical and physical properties. It is therefore evident that there is a very wide range of substitution possible in the apatite structure. Steadite, with a small amount of silicon (ionic radius 0.39 Å.) replacing phosphorus (ionic radius 0.35 Å.) is one of the less complex of these substitutions.

With the small amount of data available it is not easy to account for the older analyses which, on the surface, look satisfactory. But in no case was fluorine determined, either qualitatively or quantitatively. As the older analyses were done over sixty years ago, there is probably ground for suspicion, especially in view of the analytical difficulties involved in this combination of elements. If there was no fluorine present, the crystals dealt with by the earlier authors may have been related to something like an hydroxy-apatite, or even a carbonate- or a sulphate-apatite. But there are none of these extra constituents present in sufficient quantity to support this; and it is very doubtful if sufficient water, carbonate, or even sulphate could be present in the slags at their melting temperatures to allow of the formation of these compounds.

It is much more likely that fluorine was simply not determined, its weight being added to that of the other constituents. If the crystals were dissolved in acid, and the metallic elements determined by direct precipitation, calcium fluoride would be thrown out with the Group III metals, even if phosphorus was removed first. The fluorine would be weighed with the iron, &c., and would be hidden here in the analysis. The silica determination would be low as some would be lost during the evaporation with acid. In this connexion it is interesting to note that the old silica determinations are much the same as the figures quoted above for the new analyses before the loss with fluorine was allowed for. It suggests that there may be a definite limit to the simple substitution of silicon for phosphorus. S. O. Agrell (1946) gave partial analyses of some apatites from slags. These contain about $2\frac{1}{2}\%$ silica. There is clearly no dividing line between apatite and steadite; it is probable that most slag apatites contain some silica.

There remains little doubt that all of the samples of steadite which have been examined are fluorapatites with some of the phosphorus replaced by silica. There must also be some replacement of calcium by

elements of higher valency, probably Fe^{+++} , but this does not show up in the analyses owing to the amount of extraneous oxides.

Morphology.—The crystalline form is very constant. The mineral forms long needle-like crystals of hexagonal cross-section. The prism angle is exactly 60° , so there can remain little doubt that they belong to the hexagonal system. The crystals may be up to 2 cm. in length, and 1 mm. in diameter. They are commonly a pale-brown colour, but may be colourless. There are no terminal faces apart from the basal plane (0001), and a well-marked parting or cleavage is frequently seen parallel to this face. Confirmation of the crystal system and the identity of this mineral with the apatite group was provided by powder photographs.

Optical properties.—In thin section the colour is usually pale brown. Sample A is the one exception to this. The pleochroism of the coloured samples is very weak. The birefringence is very low, and it is very difficult to obtain optic figures. Basal sections are quite isotropic, and, as far as can be seen, give a uniaxial interference figure. The elongation of the crystals shows that they are negative in sign. The refractive indices are slightly higher than those for pure apatite. Some values for various samples are given in table VIII, as well as those for artificial fluorapatite. The higher figures for the steadite are evidently due to the replacement of the phosphorus by silicon. The same effect is seen in the nagelschmidtite series.

TABLE VIII. Optical data of steadite and apatite.

	1.	2.	3.	4.
ϵ . . .	1.638	1.654	1.655	1.629
ω . . .	1.642	1.657	1.657	1.632
$\omega - \epsilon$. . .	0.004	0.003	0.002	0.003

1, Sample A. 2, Sample B. 3, Sample C. 4, Artificial fluorapatite (R. Nacken, 1912).

The most interesting phenomenon to be seen in thin section is the multiple twinning. When viewed between crossed nicols, two sets of twins are almost invariably seen in prismatic sections. One set is parallel to the basal plane, the other to the prism faces. A photograph of a single crystal showing the two sets of twins is shown in figure 6. The photograph was taken with the crystal nearly parallel to one of the cross-hairs, and clearly shows the two sets of twins at right angles. The twinning has previously been noted by Agrell (1946) and H. Schneiderhöhn (1931).

Apatite belongs to the crystal class 6/m. This class possesses one hexad axis normal to a plane of symmetry. As there are no diad axes or vertical

planes of symmetry, parallel and normal twins can be obtained simply by twinning on axes which coincide with the usual position of diad axes in the hexagonal system. Normal twins are obtained when the twin axis is normal to a composition plane which coincides with the prism faces. Continuous twinning of this form would result in multiple twinning parallel to the prism faces. Parallel twins are obtained when the basal plane is the composition face. Continuous twinning of this type will result in multiple twinning parallel to the basal plane. If both of these types of twinning were to occur, the result would be two sets of twins at right angles, one parallel to the basal plane and the other parallel to the prism faces.

The difficulty in applying this explanation to the present case lies in the fact that the twinning is most clearly seen when the crystals are parallel to the cross-hairs of the microscope, and are not visible at all in the 45° position. Simple twinning of either kind would not be visible at all in section between crossed nicols, as the effective orientation of the sectors will always be the same. It is difficult to see how such twinning

is going to be visible under the microscope unless some more complex law enters. The steadite crystals show the two sets of twins best when they are parallel to the cross-hairs, so that certain parts of the crystal are showing apparent inclined extinction (fig. 6). It is possible that the twinning has been formed by inversion from a higher-temperature form.

Acknowledgements.—The author would like to place on record his indebtedness to Professor C. E. Tilley for bringing the subject to notice, and for his supervision; and to Dr. N. F. M. Henry for his ready assistance and advice.

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FIG. 6. Crystal of steadite showing the complex cross-hatched twinning. Crossed nicols, crystal length at about 5° to the vibration direction of one nicol.

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*The use of diamond-impregnated tools for rock-slicing.*¹

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Introduction.

FOR the cutting of chips from rocks preparatory to thin-slicing, it has been standard practice for many years to use notched soft iron disks, manually armed with diamond powder. The latest machines employing cutting-disks of this type at the Geological Museum were built at the Government Training Centre, Ascot Works, Letchworth, to the design of the late Dr. H. H. Thomas and of Mr. W. Ward of the Centre. These are powered with 0.25 horse-power variable speed direct current motors, giving a maximum disk speed of 280 revolutions per minute. By means of rheostats, control of speed as sensitive as that obtainable with a treadle type of machine (see A. V. Weatherhead²) is achieved. The normal speed for cutting is 160 to 180 r.p.m. In cutting a hard rock such as chert, it may be necessary to recharge the disk with diamond several times during the operation. The rock-specimen is held in a steel clamp with hardwood liners, mounted on a swinging arm. The rock is held in contact with the disk by the tension of a spring, or, during delicate work, by the pressure of the hand. Water is employed as a lubricant for cutting, except for water-soluble minerals, when paraffin is employed. A slice-holder, designed by Mr. D. W. Hepple, which fits into the clamp, enables chips already mounted on glass slips to be sawn to a minimum thickness of about 0.3 mm. These machines have given excellent service and have been widely copied. By means of three such machines at the Museum, and one at the Edinburgh office of the Geological Survey, a total of 14,600 thin sections were made during the years 1935 to 1946. Coarse grinding during this period was carried out by means of cast iron laps using silicon carbide as an abrasive.

¹ Published by permission of the Director of the Geological Survey and Museum, and the Manager of the Government Training Centre, Letchworth.

² A. V. Weatherhead, Petrographic micro-technique. London, 1947. [M.A. 10-190.]

The development of diamond-impregnated grinding-laps was made necessary by the general introduction into machine-tool practice of tools tipped with tungsten, tantalum, and titanium carbides. Owing to its combustibility, diamond cannot be bonded with fused metal, or with vitreous bonds fired at normal kiln temperatures. The first diamond-impregnated laps to prove successful employed resinoid bonds. An application of this type of lap to rock-sectioning has been described,¹ but the rate of wear appears, from the figures quoted, to be excessive. The problem of bonding diamonds with metal was solved, shortly before the recent war, by an application of the process of powder metallurgy. In this, the diamond powder is mixed with powdered metal and sintered without fusion of the metal.² Complete laps or disks, or merely cutting surfaces may be formed in this way. Recognizing the importance to the war-effort of tools of this type, the Belgian pioneer Mr. Peter Neven was invited to this country by the Ministry of Supply in 1940, and a range of his products came on to the market in 1941-2. Probably the earliest application of metal-bonded diamond-impregnated tools to mineral subjects was to the cutting of oriented quartz oscillator plates.³

Experiments in the application of diamond-impregnated cut-off disks to rock-slicing were commenced by Dr. J. Phemister and Dr. A. G. MacGregor in 1945. The Letchworth machine at the Edinburgh office was equipped with a 6-inch diamond-impregnated cutting-disk, and the cutting speed was raised to 500 r.p.m. A positive feed was found to be necessary, and a screw control to the swinging arm, designed by Mr. J. McCall, was added to the machine. The disk here has given satisfactory service, but now shows signs of wear. In London, the construction of a new and heavier machine, capable of giving higher speeds was put in hand; details of this machine are given below.

Meanwhile in the laboratory of the Treforest sparking-plug factory operated by the K.L.G. Company for the Ministry of Supply, Mr. T. G. Jones had constructed a machine incorporating a 6-inch diamond-impregnated cut-off disk of Van Moppes manufacture, and a diamond-

¹ A. E. Alexander, Use of diamond laps in making petrographic and metallographic sections. *Industrial Diamond Rev.*, 1942, vol. 2, p. 27. Anonymous, The production of quartz crystals. *Ibid.*, 1944, vol. 4, pp. 56-58. P. Grodzinski, Diamond and gemstone industrial production methods—V. *Ibid.*, 1948, vol. 8, pp. 279-284. [M.A. 10-559.]

² H. E. Hall in J. Wulff (editor), *Powder metallurgy*. Amer. Soc. Metals, Cleveland, Ohio, 1942.

³ E. T. Larson, Now it can be told. *Industrial Diamond Rev.*, 1946, vol. 6, pp. 261-262.

impregnated grinding-lap, for sectioning sparking-plug insulators (composed of 'corundite', corundum plus lime-magnesia glass). This was in constant service for five years before the factory was closed in 1946, when the machine was purchased for the Geological Survey. It continues to give excellent service after eight years of daily mineral cutting, and the disk shows as yet no signs of wear.

The cutting portion of the Treforest machine consists of a horizontal spindle carrying the cutting-disk and a pulley, driven at 2400 r.p.m. by a flat belt from a 440-volt alternating current 0.25 horse-power motor. A lathe-type feed, mounting a hardwood-lined clamp, gives screw-controlled motion towards and across the periphery of the disk. To prevent rusting, the coolant used is water mixed with soda and soluble oil. A motorized suds pump, submerged in a tank beneath the machine, supplies the coolant to the cutting surface and to the grinding laps, and the liquid returns to the tank after use. The maximum length of cut obtainable with this machine is 1 inch.

Rock-cutting machine.

For proper efficiency and good wear, diamond-impregnated cut-off disks require to rotate at a considerably greater rate than the manually armed type. A minimum peripheral speed of 6000 feet per minute is specified by the makers. Thus they cannot be applied to the older type of cutting-machine with modification of the machine. In designing a new and heavier machine, the general layout of the Letchworth machine was retained. The cutting-disk runs horizontally and is enclosed in a zinc-lined cutting chamber having a perspex window in the cover. The machine was at first equipped with a swinging arm to carry the specimen clamp, tension being provided by weights acting through a pulley. Even at the maximum pressure recommended by the makers of the disk, satisfactory cutting of hard materials was not obtained. Benefiting from experience with the Treforest machine, a positive lathe-type feed was substituted, and this has proved completely satisfactory.

Designing of the new machine was commenced by Mr. Ward at Letchworth, but the work was later taken over by Mr. K. West and Mr. W. Shanks, who have been in charge on the drawing-office side.

The general layout is shown on fig. 1 and in the accompanying photographs (figs. 2 and 3). The cutting-disk used is a 12-inch diameter 'Neven', manufactured by the Impregnated Diamond Company Ltd., of Gloucester. The thickness of the cutting edge is 0.08 inches (2.03 mm.) and the width of the copper-bonded rim carrying the diamond powder

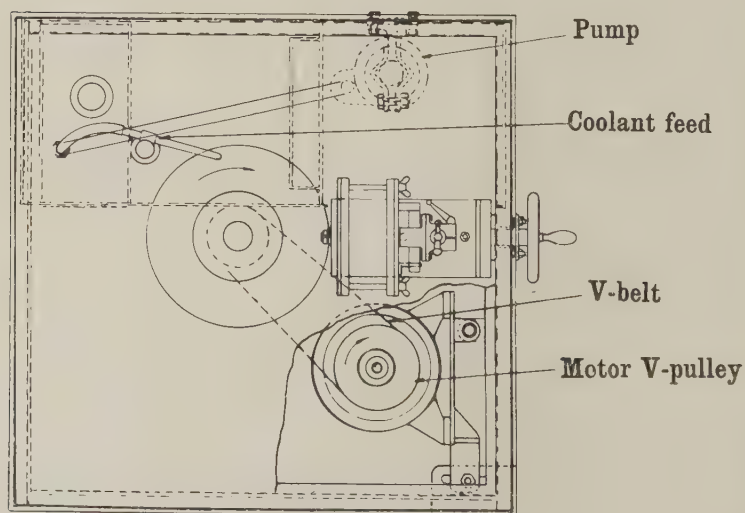
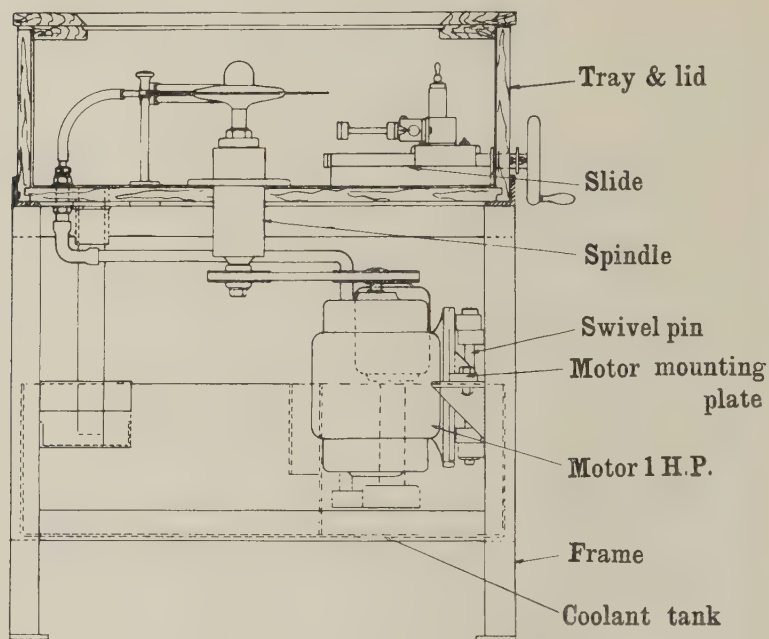


FIG. 1. Sectional drawing and plan of rock-slicing machine, to show general arrangement.



FIG. 2. Side view of rock-slicing machine with side covers removed.

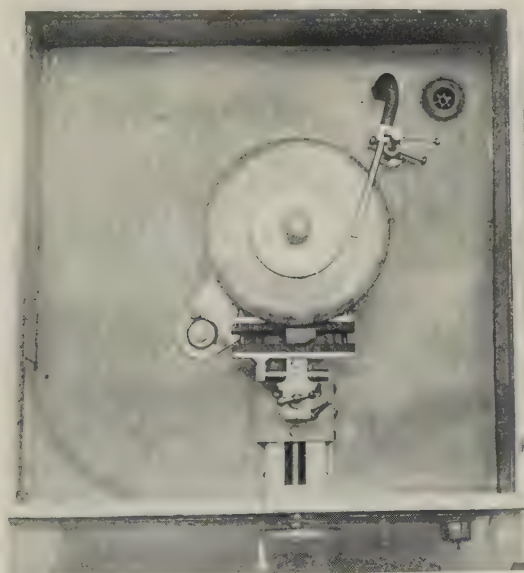


FIG. 3. Photograph of rock-slicing machine from above.

is 0.125 inches (3.15 mm.). The abrasive is 80–100 diamond grit. The disk is held by means of flanges 6 inches in diameter to a vertical spindle, to which it is locked by means of a left-hand threaded nut and cover. It may be noted that complete rigidity and absence of end-play in the spindle are essential. These are ensured by the use of a spindle one inch in diameter, carried in Skefco bearings, a roller-race and a ball-race at the top (to deal with radial and end thrust), and a single heavy-duty deep-grooved race at the bottom. The spindle assembly is carried in a fabricated steel housing, to exclude abrasive rock-particles. The races are lubricated by a grease gun. Special grease-retaining washers, supplied by Skefco, are employed on the bearings.

The spindle is driven by a V-belt from a 220-volt direct current 1.0 horsepower motor, at a normal spindle speed of 1900 r.p.m. (= 6000 feet per minute peripheral speed). A field rheostat makes provision for increasing this speed to 2200 r.p.m.

The feed mechanism provides for both vertical and horizontal movement of the specimen-holding clamp, while the clamp itself can be adjusted and set in a lateral and radial sense. The vertical movement is carried out by a screw having 16 threads per inch. This is adjusted and locked in position before the cut is commenced. Horizontal motion towards the disk is provided by a robust left-hand threaded shaft, controlled by a hand-wheel on the front of the machine. As in the older machines, the specimen is carried between wood-lined jaws which grip it tightly; the smallest movement of the specimen during cutting might lead to damage to the cutting-disk.

The lubricant employed for cutting is water with 30 fluid ounces of soluble oil and 1 pound of soda per 9 gallons. This is delivered to the cutting surface by jets above and below the cutting-disk, fed from a Varley type GS.455B submerged centrifugal suds pump installed in a tank in the lower part of the machine. The used coolant passes over a weir to allow rock particles to settle before it is returned to the tank. The cover of the cutting chamber is closed during operation, and observation is facilitated by means of a hand-windscreen wiper.

Performance.

All but very friable subjects can be cut by means of the high-speed machine. A series of tests carried out by Mr. D. W. Hepple and Mr. G. H. Collins gave the comparison between the times taken to cut a 1-inch square chip from the same specimen by the manually armed and diamond-impregnated disk, which are summarized in the table below:

Comparison of times taken to cut a 1-inch square chip, in seconds.

Rock.	Manually armed disk.	Diamond-impregnated disk.
Chalk flint	840*	13
Hornfelsed diabase, Penlee, Cornwall .	530	16
Quartz-enstatite-diabase, Penmaenmawr	323	10
Limestone, Frosterley, Durham . .	292	9
Granodiorite, Aberdeen . . .	257	11
Ankerite, Cowgreen, Durham . .	190	8
Hornfels, St. Erth, Cornwall . .	165	8

* Including 85 seconds recharging the disk.

It will be evident that there is a substantial saving in time; for the seven rocks tested, a little over 1 minute is compared with nearly 43 minutes for the older method. The maximum depth of cut obtained with the 12-inch disk is 3 inches, and specimens up to 5 inches wide can be held in the clamp, though a cut 3 inches deep over the full width is not obtainable. During tests a slice of chert 0.02 inch (0.51 mm.) thick was cut, and over the whole area of 2 square inches (12.9 square cm.) the maximum variation in thickness was found to be 0.0004 inches (0.001 mm.) by micrometer measurement. The thickness of the chip which can be cut depends, however, on the nature of the rock. Chips mounted on glass slips with Canada balsam can be cut without difficulty on the machine. With normally hard rocks, cutting to a thickness of 1 mm. presents no difficulty. On present practice, the section is taken down from this stage on a glass plate with carborundum, or on the diamond-impregnated laps described below.

The possibility of using a section-holding clamp with micrometer adjustments in lateral and radial senses is now being investigated. By this means it is hoped to cut the chip, on the glass slice, to a thickness approaching that required for the final slice (0.03 mm.). This would represent an important step towards mechanical slice-making.

The machine has, at the time of writing, been in use for two years and has made not less than 5000 cuts. The cutting-disk shows very little evidence of wear, and given reasonable care in use, it appears that a long life may be expected for this tool under rock-cutting conditions.

Grinding-machines.

Two diamond-impregnated grinding-laps are at present in use at the Geological Museum. These are mounted on metallographic polishing machines, consisting of 0.25 horse-power motors, vertically mounted,

with the laps directly carried on the motor spindles. Cast iron casings round the laps give splash protection. The laps are supplied with coolant from the tank and pump which supply the smaller cut-off disk. One of the laps, a 'Neven' of Impregnated Diamond Co. manufacture, is 4 inches in diameter, with a cutting face 1.25 inches wide. This one contains 50 70 grade diamond grit, and rotates at 3400 r.p.m. The other, an older type, is 4 inches in diameter with a cutting face one inch wide, containing a finer grade of abrasive; this lap runs at 2600 r.p.m. The laps prove very useful for trimming chips, and for the grinding stage in the case of hard rocks.

There is some evidence that wear on these is more rapid than on the cut-off disks, but in daily use, providing that a sufficient supply of coolant is provided, several years of life may be expected with confidence. Manipulation of mounted chips takes rather more skill than on the slow-moving cast iron lap, but this can soon be acquired.

Other rock-cutting machines.

Recently a rock-slicing machine based on the prototype described here, incorporating a 12-inch diamond-impregnated disk, has been brought into commercial production by Sports Machines Ltd., of 373 Regents Park Road, London, N. 1. This includes also a grinding lap. The first tests have proved very satisfactory.

It must also be mentioned that milling machines, incorporating vertically-mounted cut-off disks, are available on the market, for example, from the Impregnated Diamond Company. The addition of suitable clamps to the movable work-platform of such a machine would make it suitable for rock cutting. For sawing slices from long borehole cores such a machine would be particularly useful. The main objection to the vertical mounting is the difficulty of preventing splashing of the coolant fluid.

Conclusion.

The use of diamond-impregnated cutting-disks mounted in a suitable machine gives substantially greater speed than with the manually armed type, the time spent in charging also being saved. Where a substantial programme of slicing is undertaken, it is probable that the cost compares favourably. Larger cuts and more precise control of cutting are obtained. The cut surfaces are smooth and free from macroscopic grooves. Diamond-impregnated laps provide a means of rapid grinding. But notwithstanding the improvements here suggested in the

mechanization of slice-making, the quality of the slices produced will still depend upon the manual skill of the slice-maker.

Acknowledgements. —The co-operative work done by members of the staffs of the Government Training Centre, and of the Geological Museum, mentioned in this note, is gratefully acknowledged. Gratitude is also expressed to successive managers of the Centre who have facilitated the work. We are desired by the present manager to add that shortage of engineering students makes it impossible for him to accept further work of this sort at present.

A new type of specific gravity balance.

By SIR JAMES WALTON, K.C.V.O., F.R.C.S., F.R.C.P.

[Read March 23, 1950.]

A RAPID and accurate method of determining the density of a mineral has long been sought for by mineralogists and gemmologists. The hydrostatic method gives a high degree of accuracy, but has the drawback that each estimation occupies about a quarter of an hour so that if some ten to twenty specimens have to be investigated the time taken will be considerable. The use of heavy fluids is rapid, but for finer distinctions a large number of fluids is required and they tend, either from evaporation or chemical change, to become variable, while the Westphal balance is only reliable for fairly large portions of the mineral. Several attempts therefore have been made to develop a balance which will give a direct reading. Most of these such as the Kratschner balance have been based upon Leonardo da Vinci's principle of the bent lever, but generally have not been sufficiently delicate or accurate for small specimens. After a considerable number of experimental trials I have been able to produce a model which within one or two minutes will give a reading sufficiently accurate for all diagnostic purposes, although it might not meet the requirements of a research worker.

The instrument (figs. 1 and 2) differs from an ordinary balance in the two important particulars, that the arms instead of moving only a few degrees have to describe an arc of 90° , and the position of the centre of gravity has to be altered.

The balance consists of a central pinion or axle *A* to which two arms *B* are attached extending 32 mm. from the centre and terminating at each end in grooved quarter circles *C* around which pass silk threads suspending the pans *D* and counter weight *E*, so that the length of lever supporting the point of suspension remains constant through an angle of 90° ; attached also to the axle is a relatively long pendulum with a screw thread cut in its lower part on which the pendulum weight *F* can be moved up or down. To the upper end of the pendulum bar is screwed a counter weight *G*. It was found that this unit must be of the lightest weight possible combined with rigidity or a high modulus of elasticity so that it would not bend. After many experiments, with brass, steel,

and duralumin, perspex was used with entirely satisfactory results. The axle has a strip of safety-razor blade H running through it and fixed at an angle of 45° with the vertical. Its free ends are supported on either side in short lengths of glass tubing so that the balance rotates round the edges almost entirely free of friction. From the left arm are suspended two light pans D united by a thin tantalum wire. Below the lower one is a beaker standing on a brass stage which can be rapidly raised or lowered by means of an excentric wheel. When the stage is lowered the lower pan is above the level of the fluid in the beaker, but when it is raised the pan is entirely submerged. To the right arm is suspended the counter weight E which consists of a hollow duralumin tube the top of which can be unscrewed. It contains lead filings which can be added to or removed to gain an accurate balance. The pendulum moves across a scale doubly graduated, the lower scale giving a reading of the weight up to 5 carats and the upper giving the specific gravity.

Unlike an ordinary balance it is essential that the centre of gravity of the balance arms and their appendages be below the point of suspension or the whole equilibrium is disturbed. This point of suspension has a definite position which is given by the following equation. The length of the balance arm multiplied by the highest weight to be measured on the scale equals the weight of pans, balance arms, and counter weight multiplied by the height of the point of suspension above the centre of gravity. In fig. 2.3, L is the length of the balance arm, and x the height of point of suspension above the centre of gravity; W is the weight of the pans, balance arms, and counter weight, and the highest weight to be measured is 6 carats. Then $Wx = 6L$. Since W and L are easily measured, x can readily be obtained. With the pendulum unit absent and 6 carats in the scale the balance will then swing round until the centre of gravity and the point of suspension are in a horizontal line. In this position the system is, however, unstable, for, whether the centre of gravity moves farther up or down, the moments around the point of suspension will be decreased. Therefore only $\frac{5}{6}$ of the scale, i.e. 5 carats are used, and a stop is placed above so that the pendulum cannot swing far round. It is clear that the point of suspension will only be a short distance above the centre of gravity; in my own model it was 2.25 mm., and it is inversely proportional to the weight of the perspex unit and its appendages. It is for this reason that the unit must be as light as possible or one would be unable to measure and drill accurately the canal for the insertion of the razor blade strip.

The pendulum weight F is an inverted T-shaped piece of metal which is drilled and a screw thread cut to fit the screw on the lower end of the pendulum. It is made of a convenient size and the edge milled for ease of turning. It is placed in a convenient spot on the lower end of the pendulum which is then balanced on a knife edge placed at the point

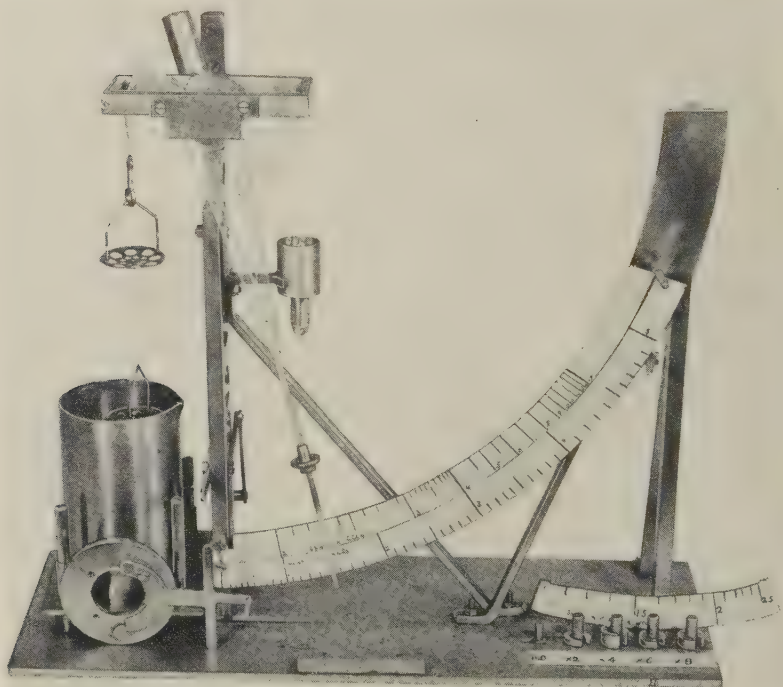


FIG. 1. A new type of specific gravity balance. The upper scale gives sp. gr. 2-15, using carbon tetrachloride. The lower scale gives weights 1-5 carats. The smaller supplementary scale gives sp. gr. 1-2.5, using water.

of suspension of the balance arm; the counter balance G being cut to give an accurate balance; its weight can be roughly estimated by taking moments around the point of suspension, but the final adjustment has to be made experimentally.

The correct balance of the pans and wire with their counter weight E is found by weighing them against one another on a balance, lead filings being added to or removed from the counter weight as required. The pendulum is then permanently fixed to the axle with a cement made of

perspex dissolved in chloroform (fig. 2.4). With the lower pan in the fluid (carbon tetrachloride is used as it is easily obtainable and has a low surface tension) a 5-carat weight placed in the upper pan should make the pendulum swing round and come to rest at a point representing five-sixths of the quarter circle, i.e. 75° from the vertical; this may require

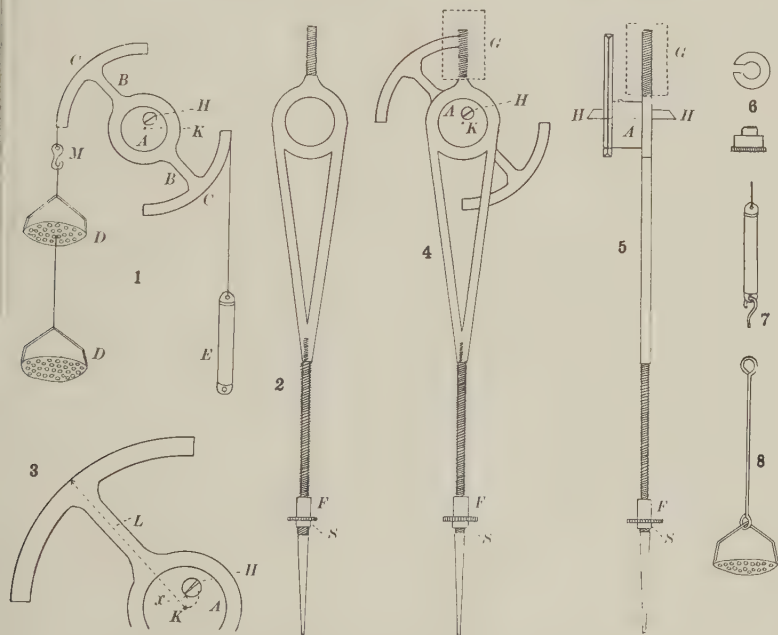


FIG. 2. Parts of the specific gravity balance, (1) arms, pans, and counter weight; (2) pendulum; (3) razor-edge pivot of arms and pendulum; (4) assembled perspex unit, front view; (5) same, side view; (6-8) accessories.

a slight adjustment of the height of the pendulum weight F . When this is correctly adjusted the stop S is screwed up to it and then permanently fixed with perspex cement, so that when the pendulum weight is screwed down to it the pendulum will always be vertical and register 0° when the pans are empty and 5 carats when that weight is placed in the upper pan. It is now only necessary to calibrate the two scales.

To use the instrument the pendulum weight is screwed down to the stop, and the beaker raised so that the lower pan is submerged. The pendulum will now register 0° . The mineral is placed in the upper pan when the pendulum will swing up to give the correct weight. The

pendulum weight is now screwed up and as this is done the pendulum will swing up the scale so that it can be made to stop exactly opposite the 5-carat mark. Thus whatever the weight of the specimen (under 5 carats) it is made to measure 5 unknown units. The pendulum is moved back to 0° , the beaker lowered, the mineral removed from the upper to the lower pan, the beaker raised, and the pendulum freed. When it comes to rest it will give an accurate reading of the density on the upper scale.

Since the weight of fluid displaced is always a given proportion of the weight of the mineral it will be seen that if the weight is always given as 5 units, which with each specimen will have different values, the specific gravity will always be given in its correct position on the scale, e.g. if a mineral of sp. gr. 2 is weighed in water it will lose half of its weight whatever that may be, so that if its weight be given as 5 units of some sort, its specific gravity will be at a point corresponding to 2.5 on the weight scale. If its sp. gr. is 4 it will lose $\frac{1}{4}$ of its weight so that the sp. gr. of 4 will be opposite the 3.75 on the weight scale. The principle of the instrument is then, that after the weight in carats has been recorded the pendulum weight is raised so that the value of the unit of weight is altered until the specimen weighs exactly 5 of these units.

As described above the limit of weight of the specimen to be investigated is 0.5 carats, the lower practical limit is however 1 carat. If for instance a specimen of $\frac{1}{2}$ carat is being investigated the weight will be correctly given, but when the pendulum weight is screwed up so that the pendulum moves to the 5-carat mark each major division of the scale will equal $\frac{1}{10}$ carat and the smaller divisions $\frac{1}{100}$ carat. With such a delicacy the resistance of the fluid on the pan and specimen will cause considerable inertia and the pendulum will move so sluggishly that the recording of the specific gravity is unreliable. With such small specimens the use of heavy fluids is still the most satisfactory method. In the upper limits the 5-carat range will cover the greater number of gemmological specimens, but some of them and many mineralogical specimens will be of greater weight. Four extra graduated weights are therefore provided. They are slipped on to the pendulum weight (fig. 2.6) and are such that when in position the recording on the weight scale has to be multiplied by 2, 4, 6, 8 respectively so that in each case the limit of weight will be 10, 20, 30, and 40 carats. Naturally the larger the weight added the less delicate will be the recording; the specific gravity scale will, of course, remain unchanged. The only factor that is altered is the unit of weight.

The specific gravity of the fluid used, carbon tetrachloride, is 1.6. Certain substances, of which the most important to the gemmologist are opal, amber, tortoiseshell, jet, vegetable ivory, and the plastic imitations (bakelite, erinoid, and celluloid), have a specific gravity less than this and would float off the pan. In such cases the beaker must be filled with distilled water instead of carbon tetrachloride. Immersed in it the lower pan will weigh more than when immersed in carbon tetrachloride. A small extra counter weight in the form of a wire hook is hung on the lower ring of the duralumin counter weight (fig. 2.7) and will give a correct balance, the weight scale will then remain correct. The specific gravity scale will, however, differ considerably, for the proportion of the weight lost in water will be less, a small extra specific gravity scale registering up to 2.5 is therefore provided which will slip over the lower part of the upper scale.

For the use of those who simply require a rapid method of estimating the weight, a single pan (fig. 2.8) is made which hangs on the hook *M* (fig. 2.1) instead of the double pan and accurately balances the counter weight. The beaker is removed, the specimen placed in the pan, and the pendulum released when it will swing over and give a correct reading of the weight thus avoiding trial with several weights as in an ordinary balance.

The instrument is being manufactured for me by Messrs. Rayner and Keeler of 100 New Bond Street, London, W. 1.

A method to determine the indicatrix of small crystals.

By N. JOEL

Birkbeck College Research Laboratory, London.

[Communicated by Dr. F. A. Bannister; read January 26, 1950.]

Introduction.

IN the course of the investigation of the crystal structure of sodium-thyroxine-*dl* it appeared to be necessary, in order to find the approximate orientation of the molecule, to determine the orientation of the indicatrix and the values of the principal refractive indices.

The crystals are flat and very thin (about 0.03 mm. thickness), and when put on a glass slide they all lie on their (100) face. This suggested the use of the universal stage, but the high birefringence of the crystals prevented it from giving good results. Moreover, as the crystals belong to the triclinic system and have no regular contour, it would have been difficult to refer the indicatrix to the unit cell. The interference figures seen when the crystals lie on a glass slide were mis-oriented, though sufficient to determine the sign of the indicatrix, and no clear interference figures could be seen when the crystals were far from horizontal.

To overcome these difficulties the method which follows was developed, and proved to be very useful for all uniaxial crystals and highly birefringent biaxial crystals, whatever their habit.

The one-circle stage goniometer.

The crystal is mounted on a glass fibre (no particular orientation is necessary) at the end of the one-circle stage goniometer described by Bernal and Carlisle¹ (fig. 1). It is a very simple instrument, fits on any microscope stage, and enables one to rotate the crystal about a horizontal axis. Furthermore, a thin glass slide may be adjusted to the goniometer, underneath the crystal, and a drop of a liquid that does not attack the crystal and has a suitable refractive index may be put on it, so as to have the small crystal completely immersed. The mounting of the crystal has to be done carefully, so as to enable its free rotation in the liquid, not far from the glass slide but without touching it.

¹ J. D. Bernal and C. H. Carlisle, *Journ. Sci. Instruments*, London, 1947, vol. 24, p. 107.

The end of the crystal holder *A* of the goniometer may be unscrewed and adapted to the holder of an X-ray diffraction camera, without changing the mounting of the crystal. As will be seen later, this makes it very easy to refer the axes of the indicatrix to the unit cell of the crystal, and also enables one to use this method as a help for setting crystals for X-ray diffraction photographs.

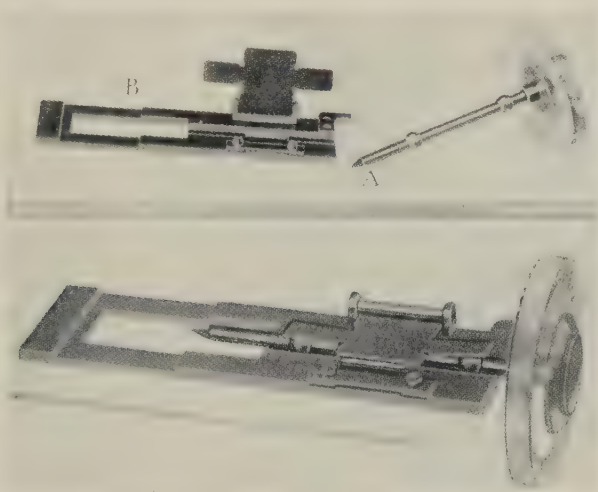


FIG. 1. The one-circle stage goniometer. (Reproduced from the Journal of Scientific Instruments.)

General considerations.

When a crystal is in a given position (on a polarizing microscope, crossed nicols, parallel light), the two observed extinction directions are the axes of the ellipse determined by the intersection of the indicatrix with the plane of the microscope stage, and the magnitudes of these axes are given by the corresponding two refractive indices. Errors arise if the incidence is not normal, due to the deviation of the wave-front, and especially if the crystal has a complex habit. No such errors appear when the crystal is immersed in a liquid whose refractive index is equal to that of the crystal in the observed vibration direction.

Now, for each position (θ) of the goniometer, there are two extinction directions (ϕ_1 and ϕ_2 perpendicular to each other), given by the corresponding readings of the microscope stage, or polarizer-analyser system in some models. These extinction directions can be represented on a

stereographic projection at suitable intervals of θ (fig. 2). The primitive is the great circle $\theta = 0^\circ$, and on it the two ϕ readings for the initial position of the crystal are marked, taking as origin the intersection of the primitive with the rotation axis of the crystal. The whole is adjusted so that when $\phi = 0^\circ$ the light transmitted by the polarizer vibrates parallel to the rotation axis of the crystal.

If the goniometer is now turned by a given angle, for instance, 10° , the great circle $\theta = 10^\circ$ will come into the horizontal, and there will be the two corresponding ϕ readings.

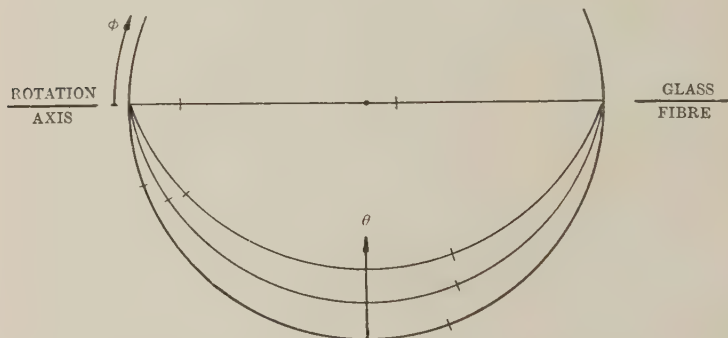


FIG. 2. Extinction directions in stereographic projection. The great circles $\theta = 0^\circ, 10^\circ, 20^\circ$, and 90° are shown, with the two extinction directions on each.

In the stereographic projection, each value of θ is represented by a great circle through the goniometer axis; and on those great circles, with the help of a stereographic net, the ϕ readings are inserted. The angle θ is measured in the sense opposite to that of the rotation of the crystal, the sense of ϕ depending on the geometrical arrangements. During a complete rotation of the indicatrix about its fixed (but arbitrary) axis, these two sets of points determine, on the indicatrix and on the stereographic projection, a centro-symmetrical set of curves.

It is clear that every vector of the indicatrix will eventually come into the horizontal plane during this rotation; hence, it is possible to bring into the horizontal plane each one of the three axes in turn.

As each axis of an ellipsoid is a two-fold axis, every central section that contains one of the three axes has this axis as an axis of symmetry. This is particularly easy to see for the X and Z axes. As γ along the Z axis is the longest vector of the ellipsoid, it must also be the longest vector of any ellipse that contains it, and hence, is the longer axis of that ellipse. The same argument applies to the X axis, α being the smallest refractive

index. It follows that, as soon as one of the three axes of the indicatrix comes into the horizontal plane, it becomes one of the two axes of the observed ellipse, and therefore the points representing the three axes of the indicatrix lie on the curves of the extinction directions. In other words, that set of curves contains the points representing the axes X , Y , Z of the indicatrix.

The axes will be located if the position of one of them is determined. That may be done by finding the particular vibration direction in the crystal for which the refractive index is a maximum or a minimum.

Experimental procedure.

There are two independent steps: (a) the determination of the stereogram of the extinction directions, and (b) the determination of the direction of maximum (or minimum) refractive index.

(a) From the above considerations and the study of fig. 2, it is quite clear how the stereogram may be drawn, taking θ at suitable intervals, for instance, 10° . During this operation, which requires only a very short time, there is no liquid on the goniometer glass slide.

(b) To find the direction of maximum (or minimum) refractive index, a drop of a suitable liquid of known refractive index (near to the one expected to be found for the crystal) is put on the glass slide of the goniometer, so as to have the small crystal completely immersed in it. By successive rotations of the goniometer, and by putting the crystal each time in extinction position, the vibration direction (or directions) for which the crystal has a refractive index equal to that of the liquid is determined with the method of the Becke line. It is easy to discover now (also with the Becke-line effect), on which side of the determined vibration direction the refractive index increases (or decreases), or in which region between two determined directions of equal refractive index the maximum (or minimum) has to be found, and a liquid of higher (or lower) refractive index is tried, after having carefully removed the first one with a filter paper, without touching the crystal. This is repeated—in general two or three attempts will be sufficient—till the maximum (or minimum) is found with the help of standard liquids or mixtures of them if necessary. This gives us, at the same time, the direction of the axis and the value of the corresponding refractive index.

Biaxial crystals.

Let us discuss the case of a positive crystal, in which the direction of the Z axis (γ) is determined first. (On a negative crystal it is better in

general to start with the X axis (α), the minimum refractive index direction.) The direction of the Z axis (θ and ϕ) is put into the stereographic projection and the great circle perpendicular to it is drawn (fig. 3). This circle will intersect the extinction direction curves at points (90° away from each other) that are the X and Y axes of the

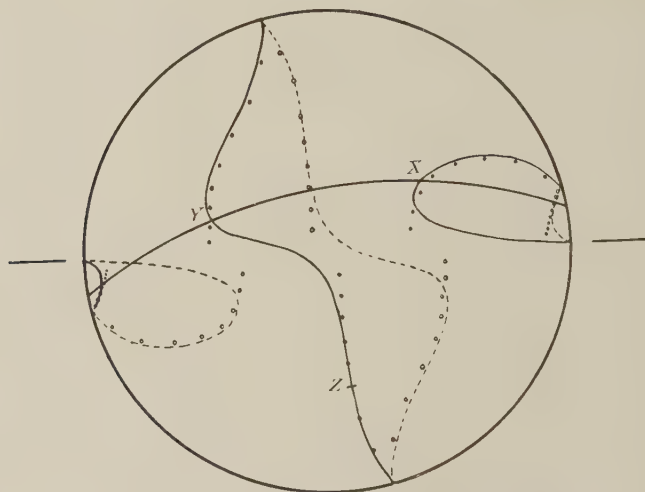


FIG. 3. Extinction directions in a biaxial crystal. Experimental points (crystal rotating in air), and theoretical curves. Also the great circle perpendicular to Z is shown.

indicatrix. Hence, it will be sufficient to determine the extinction directions in the region perpendicular to the Z axis. In some favourable cases, only a small number of points is required (it depends on the particular rotation axis of the crystal) but, even if the whole indicatrix is explored (θ from 0° to 180°), it takes only a very short time.

The X and Y axes are thus determined; and each one of them is brought into the horizontal plane, to measure α and β respectively. The direction of the X axis will be checked when measuring α , as it must be the minimum refractive index direction.

Now, X-ray diffraction photographs will enable the axes of the indicatrix to be referred to the unit cell of the crystal. For this purpose, the end of the crystal holder of the goniometer is unscrewed, and adapted to the holder of a diffraction camera, without changing the relative positions of the crystal, the glass fibre, and the end of the holder.

It should be noted that the experimental points in the stereogram of fig. 3 are affected by errors due to the deviation of the wave-front when incidence is not normal. But, when the direction of the axes and the magnitude of the indices are being determined, the crystal is immersed in a flat drop of a liquid whose refractive index is the same as that of the crystal in that particular vibration direction. Thus the wave-front travels through the crystal without the slightest deviation whatever its external shape. It is worth while to remember that on a universal stage this condition is not fulfilled, the refractive index of the hemispheres and other accessories being only near to that of the crystal.

It follows that the determination of the X and Z axes is free from errors involved in earlier steps; and the same applies to the Y axis, as it is simply the perpendicular to the plane defined by the other two.

Fig. 3 also shows the theoretical extinction direction curves for that particular mounting, drawn after the orientation of the axes and the values of the refractive indices had been found. As Professor Bernal has pointed out, they are the locus of the points of contact between the constant refractive index curves and a great circle rotating about the crystal's rotation axis. They are given here only for the purpose of comparison; the corresponding formulae and mathematical considerations will appear in another paper.

The difference between the theoretical and the experimental curves is not important as the X and Z axes are determined in optimum conditions, as explained above. That difference may be decreased if during the determination of the extinction directions the crystal is immersed in a liquid of refractive index near to the expected mean refractive index of the crystal; but it is not necessary, in general, to do so.

Uniaxial crystals.

The same general considerations apply, but the stereogram is much simpler. For every position of the crystal, one of the extinction directions is a vector lying in the equator of the indicatrix. As a result, a great circle appears in the stereographic projection, and its pole gives the direction of the axis (fig. 4).

The actual procedure is this: the stereogram of the extinction directions is drawn in order to get some idea of the orientation of the equator (only a few points are necessary). Next, the value of ω is determined and at the same time the position of the equator is defined, as the

wave-fronts are now travelling without deviation. The pole of this great circle is drawn on the stereogram, and the axis found thereby is brought into the horizontal plane to measure ϵ .

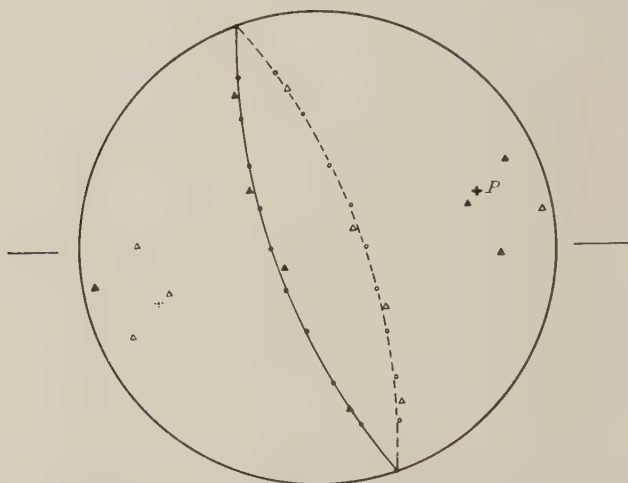


FIG. 4. Extinction directions in a uniaxial crystal. The triangles represent points obtained with the crystal rotating in air. The circles represent points obtained with the crystal rotating in a liquid of refractive index equal to ω . Also the equator and its pole P are shown.

Discussion of the results.

The value of the refractive indices obtained are as accurate as in any other immersion method, better results being obtained with monochromatic light, stabilized temperature, &c. The same applies to the optic angle calculated from these indices.

For the accuracy of the direction of the axes of the indicatrix there is a substantial difference between uniaxial and biaxial crystals.

In uniaxial crystals the errors are only those introduced by the mechanical behaviour of the goniometer and those due to the use of the stereographic net. So, it is easy to find the orientation of the indicatrix within $\frac{1}{2}^\circ$, the only condition being that the extinction directions should be observable.

In biaxial crystals the situation is different. Since the direction of the Z (or X) axis is determined as the direction of maximum (or minimum) refractive index, the accuracy depends on the rate of change of the observed index when the crystal is rotated. Consequently, the accuracy

becomes greater, the greater the value of $\gamma - \beta$ ($\beta - \alpha$ in a negative crystal).

As an example of a biaxial crystal, the indices of the crystal of sodium-thyroxine-*dl* are: α 1.65, β 1.69, γ 1.79 (sufficient accuracy for the particular crystal structure work). Thus, $\gamma - \beta = 0.10$. And it was possible to find the orientation of the Z axis within an error less than 1° , probably about $\frac{1}{2}^\circ$. The error in the orientation of the X axis is not more than 1° . As a result for the Y axis the error is also of the order of 1° . Certainly, this degree of accuracy is due to the very high birefringence of the crystal.

The method is sufficiently accurate for most purposes if

$$\gamma - \beta \text{ (or } \beta - \alpha) > 0.04;$$

and becomes accurate to about $\pm 1^\circ$ if

$$\gamma - \beta \text{ (or } \beta - \alpha) > 0.06;$$

these conditions are rather elastic and the accuracy increases with increasing values of the difference.

If, by chance, or after trial, the Y axis of the indicatrix is nearly parallel to the axis of rotation of the crystal, in the above conditions $\gamma - \beta$ (or $\beta - \alpha$) may be changed into $\gamma - \alpha$. This will make much wider the field of application, and increase the accuracy.

For uniaxial crystals, as already explained, the accuracy is independent of the birefringence.

Conclusion.

The method described has the advantage that no expensive instruments are needed; it only requires one crystal, whatever its habit may be; and it gives both the orientation and magnitude of the indicatrix at the same time. Its main characteristic is that the crystal is rotated in the liquid till in a given vibration direction its index is found to be equal to that of the liquid. This saves many changes of liquid, as has to be done when fixed crystals are in random positions on a glass slide (usual method of dealing with triclinic crystals). As already pointed out, it is a great help for relating the optical directions to crystallographic directions, and may save time in the setting of crystals for X-ray diffraction, particularly uniaxial and orthorhombic ones. For this purpose it may be used in combination with any of the X-ray methods for setting crystals described by Hendershot,¹ Weisz and Cole,² and Jeffery.³

¹ O. P. Hendershot, *Rev. Sci. Instruments* (Amer. Physical Soc.), 1937, vol. 8, p. 436.

² O. Weisz and W. F. Cole, *Journ. Sci. Instruments*, London, 1948, vol. 25, p. 213.

³ J. W. Jeffery, *Acta Cryst. Cambridge*, 1949, vol. 2, p. 15. [M.A. 10-525.]

I wish to thank Dr. W. Campbell-Smith, C.B.E., Keeper of Minerals in the Natural History Museum, and Dr. F. A. Bannister (Natural History Museum) for valuable help and encouragement; and most especially Professor J. D. Bernal, under whose direction my X-ray crystal analysis work is being done, and to whom I am deeply indebted for advice in the revision of this paper.

Some unusual alkali-felspars in the Central Australian charnockitic rocks.

By ALLAN F. WILSON, M.Sc.

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formerly of Department of Geology, University of Adelaide,
South Australia.

[Taken as read March 23, 1950.]

I. INTRODUCTION.

DURING a universal stage investigation of the pegmatitic felspars in the Central Australian charnockites, several alkali-felspars were found which, according to the stereograms published by Emmons (3, pl. 12), should have been near 'anorthoclase' in composition. This identification, based purely on optical properties, was questioned in the first instance because of the absence of other evidence for a soda-rich suite of minerals in these apparently potassic pegmatites. Two felspars which suggested a high soda-content were chemically analysed. Neither proved to be notably high in soda.

II. MICROCLINE-MICROPERTHITE WITH CROSS-HATCHED TWINNING (4750).¹

This mineral occurs in the central part of a narrow pegmatite which cuts charnockitic granodiorite 2.8 miles N. 37° E. of Ernabella in the Musgrave Ranges. Excepting the dolerites, this pegmatite is representative of the latest phase of igneous activity in this region. Associated minerals are haematite, zircon, biotite, hornblende, and tourmaline (a rare mineral in the Musgrave Ranges). No orthite was seen, as this mineral appears to be confined to somewhat earlier pegmatites of the same batholith (10, p. 208). The felspar is a very pale flesh-coloured perthitic microperthite with the perthite recognizable in hand-specimen only on careful scrutiny. The mineral fluoresces pink under intense ultra-violet radiation of wave-length 2537 Å. Under the microscope the felspar is found to contain 18 % by volume of perthitic material arranged in the normal way.

¹ Numbers refer to specimens in the mineral collection of the University of Adelaide.

Optical properties.—Work with the universal stage gave the amount of rotation needed to obtain α , β , and γ from the readings of α' and β' on (010) and α'' and γ' on (001). With use of Emmons's refractive index variation diagram (3, pl. 10), the appropriate corrections were obtained. In both specimens 4750 and 4760 these are very small, being of the order

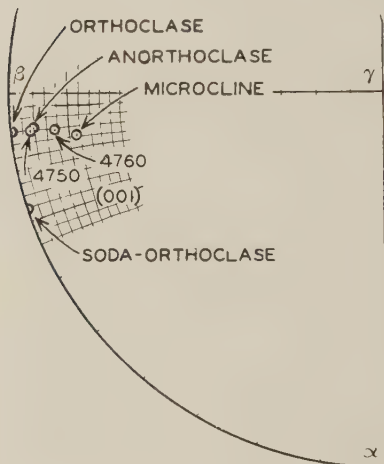


FIG. 1. Portion of stereogram showing pole of (001) for the analysed feldspars (nos. 4750 and 4760) in relation to that of anorthoclase, microcline, orthoclase, and soda-orthoclase, (after Emmons. 3, pl. 12). Neither feldspar is as soda-rich as the stereogram suggests. No. 4760 is an untwinned microcline.

of 0.00003 for (010), and 0.00006 for (001) readings. The corrected values were checked by comparison of calculated and measured 2V, and some by direct measurement. Even so, it is doubtful whether the readings can be more accurate than ± 0.0003 . Hot-water control was used in conjunction with a modern Bellingham-Stanley Abbe refractometer.

Interference figures in convergent light on (010) flakes are more off-centred for microcline than for the albite of the perthitic veins. 2V was measured with the universal stage on both (100) and (010) sections. Stereographic plots of poles of cleavages visible on (010), (001), and (100) fall near 'anorthoclase' in all cases, although the mineral is not soda-rich (fig. 1).

Extinction angles on (001) and (010) are set out with the other data in table I. The extinction angle on (001) is much smaller than the so-called usual extinction of 15° of microcline. A regular and very fine cross-hatched twinning is seen on (001).

Chemical analysis.—The analysis was carried out primarily to confirm or otherwise the high soda-content of this feldspar, and for this purpose it was considered unnecessary to attempt the tedious separation of the perthite from the micropertthitic material. The analysis was carried out on a 0.5-gram sample of powder. Alkalis were determined on a separate 0.5-gram sample by fusion with anhydrous BaCl_2 and CaCO_3 and subsequent precipitation of K_2PtCl_6 . Total iron was determined on another 0.5-gram sample. The analysis and calculations based thereon appear in table I.

The composition of the original feldspar (i.e. before exsolution of the perthite and microperthite) was Or 74.72, Ab 22.91, An 2.37. Modal percentages were measured by the Rosiwal method in sections cut parallel to (010), (001), and (100), and the average taken after recalculation to 100% to eliminate 2.2% of quartz and epidote. The values are microcline-microperthite 81.5%, perthitic albite 18.5%. The figure for microcline-microperthite is in excess of the Or as calculated from the analysis. This is due to the difficulty of measuring modal proportions on microperthitic material as well as of possible incomplete exsolution. It is clear, however, that the stereograms and other optical properties are misleading when they suggest that this microcline (which is rather rich in potash) is almost pure anorthoclase.

TABLE I. Chemical analysis and optical data of two Central Australian microclines. (Analyses by A. F. Wilson.)

4750. Perthitic microcline-microperthite, near Ernabella, Musgrave Ranges.									
4760. Untwinned microcline-microperthite, Koli-Koli rock-hole, Musgrave Ranges.									
			4750.	4760.				4750.	4760.
SiO ₂	...	...	64.95	64.66	Or ...	...	...	74.72	60.53
Al ₂ O ₃	...	...	20.11	20.10	Ab ...	...	...	22.91	35.59
Fe ₂ O ₃	...	...	trace	0.35*	An ...	...	...	2.37	3.88
CaO	...	...	0.45	0.60	Sp. gr.	...	...	2.565	2.569
MgO	...	...	trace	0.12	α ...	...	...	1.5178	1.5210
BaO	...	...	nil	nil	β ...	...	...	1.5209	1.5247
K ₂ O	...	...	11.85	10.19	γ ...	...	...	1.5232	1.5273
Na ₂ O	...	...	2.55	4.21	$\gamma-\alpha$...	...	...	0.0054	0.0063
MnO	...	...	nil	trace	2V $_{\alpha}$ (obs.)...	...	...	81° ± 1°	80° ± 1°
Loss	...	...	0.12	0.11	2V $_{\alpha}$ (calc.)...	...	...	81° 20'	79° 26'
					Extn. on (010)	...	...	4½°	5½-6°
					Extn. on (001)	...	...	5°	4-5°
			100.03	100.34					

* Total iron, mainly ferric.

III. UNTWINNED MICROCLINE-MICROPERTHITE (4760).

This mineral occurs in a narrow pegmatite in the gneissic and granulitic charnockites at the Koli-Koli rock-hole, 6½ miles WSW. of Ernabella in the Musgrave Ranges (10, p. 208). The pegmatite contains hornblende, haematite, and the weakly radioactive minerals zircon and orthite. The pegmatite is one of those responsible for the feldspathization of the rocks of the Koli-Koli ridge, and is typical of many such concordant veins among the gneissic charnockites. The feldspar in the pegmatite is very variable in colour (pale dove-grey to purplish-grey) and possesses a marked moonstone schiller. No perthitic veins are present, although along certain cracks a much later bleaching has taken place yielding

albitic material. The feldspar is non-fluorescent under intense ultra-violet radiation of $2537\text{\AA}$. The mineral is an untwinned microperthitic microcline.

Under the microscope the feldspar is found to contain a large number of microperthitic inclusions. These are best seen on (010) cleavage flakes, and an attempt was made to estimate (by the Rosiwal method) the proportions of the two feldspars. These exsolution lenses of albite appear to comprise about 40 % by volume of the microperthite. On (010) the lenses are usually 0.3×0.006 mm. and tightly packed with about one hundred bands per mm. On (001) the microperthite is less regularly spaced. Some lenses measure 0.04×0.02 mm., but most appear as wisps only 0.02×0.002 mm.

Non-feldspathic inclusions are important in this microcline. On (010) tiny dark inclusions occur in the albite exsolution lenses. About twelve grains appear in each lens and each grain is about 0.004 mm. in diameter. The inclusions probably amount to between 2 and 3 % of the total mineral. They are reddish and almost opaque, but are probably an iron-rich silicate rather than haematite, since only 0.35 % of Fe_2O_3 was found chemically. It seems likely that the iron was held in solution by the original alkali-feldspar (a soda-orthoclase?) but preferred to follow through with the soda component when exsolution of the microperthitic material took place (the potash component is free from the inclusions). Later cooling (and perhaps diminished pressure) has apparently caused this iron compound to exsolve from the microperthitic albite lenses.

Optical properties.—Refractive indices α , β , and γ were determined as in no. 4750. Owing to the confused mass of microperthitic particles on (001) sections the measurement of γ is the least reliable. However, calculated and measured $2V$ are in good agreement. In convergent light the obtuse bisectrix is somewhat off-centred on (010) flakes. If this untwinned alkali-feldspar were orthoclase the Bx_0 would be perfectly centred. Plots of poles of cleavages visible on (010), (001), and (100) fall between anorthoclase and microcline. This is not what was expected, and also indicates that the mineral is triclinic (fig. 1). Extinction angles on (001) and (010) are set out in table I. On (001), α' : (010) is between 4° and 5° . If the mineral were orthoclase there would be straight extinction.

No undoubted cross-hatched twinning is seen on (001), although in a large number of crushings a few (001) flakes were seen with shadowy extinction resembling incipient twinning. The mineral is essentially an untwinned microcline-microperthite.

Chemical analysis.—Owing to the several coloured varieties of microcline in this pegmatite, great care was taken to select material for analysis of the same colour (dark dove-grey) and similar appearance under the microscope. Owing to the abundance of microperthitic material, no attempt was made to separate the two feldspars. The analysis was carried out as for no. 4750, and the results with calculations based thereon are set out in table I.

The composition of the original feldspar (i.e. prior to any exsolution) was Or 60.53, Ab 35.59, An 3.88. An estimation, by the Rosiwal method, of the amount of exsolved albite was undertaken (extinction of the fast ray of the lenses on (010) measured to (001) suggested a composition of Ab 92, An 8). The albite lenses comprise about 40 % by volume of the whole, which compares favourably with the 39 % by weight of plagioclase calculated from the analysis. Exsolution seems to be fairly complete and indicates that the feldspar, whose optical properties suggested a high soda-content, is notably rich in potash.

IV. DISCUSSION.

(1) *Cross-hatched twinning of microcline.*

The cross-hatched twinning of microcline seems to be a combination of albite and pericline twin-lamellae with twin-laws (010) and [010]. A monoclinic crystal with a diad axis of symmetry b and the plane of symmetry $\parallel$ (010) cannot show twinning on either of these two laws. Although the *presence* of true cross-hatching¹ in a potash-feldspar may be taken as proof of triclinic symmetry (i.e. the mineral is microcline and not orthoclase), the *absence* of such twinning on (001) cannot be taken as sufficient evidence that the feldspar is the monoclinic mineral orthoclase. In this paper alkali-feldspars are described which, although showing no cross-hatched twinning on (001), are not monoclinic. They are therefore called untwinned microclines.

Many petrologists, it appears, are not aware that untwinned microcline can exist and indeed is very common in certain rocks. It has been the custom, therefore, to accept as microcline any potash-feldspar which shows cross-hatching on (001) and to relegate all other potash-feldspars to the orthoclases. Indeed, for routine work such a criterion is useful.

Several years ago Alling (1, p. 256) drew attention to the fact that

¹ Certain highly microperthitic potash-feldspars of the charnockites may display 'pseudo-twinning' due to an intimate interlocking of exsolution lenses. The difference in relief when viewed under reduced illumination serves to distinguish these lenses from the 'true' twinning.

'the term "orthoclase" is used in a very loose manner, quite inconsistent with present-day standards'. He suggests, moreover, that 'orthoclase (nearly pure potash-feldspar without microcline characteristics) is very rare in nature'.¹ Nevertheless, it appears that many well-twinned microclines are still described as orthoclases, and most untwinned microclines are overlooked.

In a recent paper on certain alkali-felspars (Jayaraman, 4, p. 118) a pegmatitic feldspar is called a 'white orthoclase' presumably because of its lack of twinning on (001) and $2V_{\alpha} 58^{\circ}$; yet the author gives the extinction $\alpha':(010)$ on (001), not as 0° , but as $4^{\circ} 30'$. Such an extinction would suggest that the mineral is triclinic and therefore likely to be microcline. Moreover, he states that 'It shows no twinning and only in one case was a very faint incipient microcline twinning noticeable'. In two other 'orthoclases' of similar type a 'very faint cross-hatching' was noticed. The optic axial angle is low (58°) but falls on the continuation of the $2V$ 'line' for the microclines as suggested by Spencer (6, fig. 4b). The mineral, therefore, does not appear to be orthoclase but rather an untwinned (or poorly twinned) microcline. E. Spencer, however, has recorded a similar oblique extinction on (001) (5, p. 333) but in his case he found 'no trace of microcline twinning either on cleaved or ground sections' and heat-treatment suggested that the mineral was orthoclase.

It appears that in the absence of the typical cross-hatching on (001) another petrographic criterion for distinguishing between orthoclase and microcline is needed. The extinction angle $\alpha':(010)$ on (001) is often listed for microcline as 15° , but actually varies from near 15° to near 0° (usually $5-6^{\circ}$). Thus a potash-feldspar which has oblique extinction on (001) should be taken as triclinic whether or not it shows twinning on that face.

Although microclines usually have an extinction angle of $5-6^{\circ}$ on (001), some have been recorded with the angle nearly zero. If the mineral is untwinned and $\alpha':(010)$ on (001) = 0° , it should, of course, be called orthoclase, but if the mineral is cross-hatched twinned and has apparently 'straight extinction' it must still be microcline. In several finely cross-hatched twinned microclines which show a superficially straight extinction I have found an extinction which is never 0° but from 1° to $1\frac{1}{2}^{\circ}$.²

¹ Although E. Spencer (6) has since established his 'orthoclase-microperthite series', microcline seems to be the more common form.

² The (010) is the poorer of the two main cleavages in feldspar, and on (001) sections it is sometimes difficult to find satisfactory cleavages. This, no doubt, accounts for many 'anomalous' extinctions in the potash-felspars.

Jayaraman (4, p. 121), in discussing some green perthitic microperthites from India, states that mainly 'Because of the very fine cross-hatching exhibited . . . these have so far been *wrongly* considered to be microcline perthites'. 'The potash member of this feldspar appears to be an *orthoclase*. . . It shows the presence of very fine cross-hatching on (001) face, but sections or cleavages parallel to this face give *almost straight extinction* . . .' (4, p. 120) (the italics are mine). But even if the cross-hatching is a very fine variety (it is carefully described) it appears to be essentially a combination of typical albite and pericline twins. In that case the mineral is triclinic, which is further borne out by the fact that the author had to record that the extinction after all was only 'almost' straight. The author supported his claim that the mineral was orthoclase by stating that in convergent light it gave a centred obtuse bisectrix figure on (010). As a routine test this usually serves to distinguish microcline (twinned or otherwise) from orthoclase, but when the extinction is nearly straight on (001) a more critical test is needed.

I have studied with a universal stage several Central Australian feldspars similar to this Indian mineral, both as regards fineness of cross-hatching and nearly straight extinction. These on (010) show a small but marked separation of b from γ , although they gave sensibly centred obtuse bisectrix figures in convergent light. I submit, therefore, that the so-called cross-hatched 'orthoclases' are microclines.

(2) *Relations between composition and physical properties.*

Spencer (6, figs. 1 and 3) has published graphs indicating the relationship between chemical composition and refractive indices, extinction angle on (010), and optic axial angle of the orthoclase-microperthite series. After much investigation he is convinced that feldspars of this series should conform fairly closely to these relationships.

But it is apparent that no such regular relationships exist for the microclines. For most microclines the extinction angle on (010) is $5^\circ \pm 1\frac{1}{2}^\circ$, but many occur with $\alpha' : (001)$ on (010) = 1 or 2° for no apparent reason. Likewise, on (001) in both twinned and untwinned microclines there is a great variety of extinction angles, again for no apparent reason. For instance, while many microclines rich in potash have $\alpha' : (010)$ on (001) = 15° , many others of almost identical composition have values ranging from 15° to almost zero. Refractive index is a little more useful, but the increase in the indices with increase of soda-content is only a trend. There are very many examples of microclines whose refractive indices, for no apparent reason, deviate strongly from this trend. 2V,

likewise, shows a tendency to increase with the increase of soda, but there are so many anomalies that an optic axial angle determination has no diagnostic value.

(3) *The occurrence of microcline.*

The researches of E. Spencer (7, pp. 90–91, &c.), Vogt (9, pp. 64–68, &c.), and others show that the first potash-felspar to slowly crystallize at temperatures of 1100–950° C. is a schillerized orthoclase of the moonstone type. In a lower temperature range (950–750° C.) the normal microperthitic orthoclase is probably the stable form, but from 750–400° C. a primary microcline appears. While this appears to be so, in addition a microcline is very often found taking the place, either wholly or in part, of an original (but now less stable) orthoclase. Certain agents may govern this change, viz. (a) crush-metamorphism, (b) age, and (c) volatile concentration at the time of crystallization of the original orthoclase.

(a) *The role of crush-metamorphism.*—Alling (1, p. 275) has shown that microcline is common in shear zones, and suggested that careful study of the feldspars could assist in deciphering structural problems. Study of the feldspars in the great crush zones of the Musgrave Ranges (10, p. 209) shows that both poorly cross-hatched and untwinned microclines have replaced the original orthoclases in almost all cases. In some of the rocks the crushing is obviously the promoter of the twinning of microcline.

However, in other cases a potash-felspar has undergone serious crushing (as seen both in the field and under the microscope) and yet has no sign of the cross-hatched twinning. For instance, no. 4755 is a pale pink microperthitic microcline which occurs in a mylonitized medium-temperature pegmatite near the summit of Mt. Carruthers in the Musgrave Ranges. No cross-hatched twinning is seen on (001) although there is ample evidence of considerable crushing. The extinction angle on (001) is very large ($16\frac{1}{2}$ –19°), and on (010) the obtuse bisectrix is well off-centred.

Alling (1, p. 292) observed that the process of section grinding could develop the cross-hatching of microcline. It is doubtful whether this is very common.

(b) *The role of age.*—In large areas of the Australian pre-Cambrian shield alkali-feldspars in igneous bodies which appear to have been emplaced ‘magmatically’ have been free from noticeable crushing since their initial crystallization. The original orthoclase-microperthite in many cases shows on (001) a peculiar wavy extinction ‘with incipient

cross-hatched twinning) departing in places from the 0° of orthoclase to about 6° . This transformation from orthoclase to a poorly twinned microcline is best attributed, for the time being, to the 'ageing' of these ancient and stable rocks.

(c) *The role of volatiles*.—Empirically a relation is suggested between the ease of transformation of orthoclase to microcline and development of cross-hatched twinning, and the ability of volatiles to enter into the structures of minerals formed at the time of crystallization of the original orthoclase.

In deep-seated rocks with no obvious signs of shearing it appears that the original orthoclase has crystallized in the presence of 'dry' minerals like hypersthene and diopsidic augite, it inverts on ageing to an untwinned microcline. The extinction angle on (001) is inclined (about 5° is common) and in convergent light the obtuse bisectrix is off-centred with the optic axial angle usually several degrees larger than the corresponding original orthoclase. Such untwinned microclines may develop a ragged cross-hatching due to subsequent crushing. This is seen in the charnockitic granites and granodiorites of Ernabella in the Musgrave Ranges.

In the cupola facies of the same 'batholith' (e.g., Bald Hill, 14 miles east of Ernabella) the original orthoclase has crystallized in the presence of hornblende and biotite (both 'wet' minerals). These orthoclases, though unstressed, have inverted to microclines which are finely cross-hatched on (001). This cross-hatched microcline displays a notable pink fluorescence under 2537 Å. radiation, whereas the untwinned or poorly twinned microclines and original orthoclases of the major igneous body do not fluoresce. This indicates that the pressure-temperature conditions which allowed the volatile to enter into the structure of the ferromagnesian minerals in the cupola facies may have allowed some trace element to enter into the structure of the original orthoclase, thus leading to a distorted structure on cooling, and a more facile inversion to a cross-hatched twinned and fluorescing microcline.¹

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¹ These and other fluorescence phenomena are treated more fully in the following paper (p. 225).

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Fluorescent felspar and zircon as petrological aids.

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I. INTRODUCTION.

ALTHOUGH there have been many publications on the fluorescence of minerals in ultra-violet light, very little systematic work has yet been done in utilizing this property for the elucidation of petrological problems.¹ The response of various minerals would seem to be entirely capricious; but the extensive work done on phosphors shows that this depends on the presence of traces of impurities. The spectacular display given by certain minerals has made a strong appeal to amateur collectors.

In 1943 the present writer made use of a fluorescent variety of zircon to assist in the subdivision of the Archaeozoic gneisses and igneous rocks of the Musgrave Ranges in Central Australia; and after further field-work preliminary observations were published in 1947.²

II. TECHNIQUE.

Short-wave ultra-violet radiation (2537 Å.), as supplied by the 'mineralight', has been found most suitable for this work. In the thousands of specimens studied neither potash-felspar nor zircon gave any fluorescence under long-wave radiation 3650 Å.

1. *Zircon*.—A number of rocks have been crushed, and the minerals heavier than bromoform studied under ultra-violet radiation. This

¹ H. Haberlandt and A. Köhler, Über die blaue Fluoreszenz von natürlichen Silikaten im ultravioletten Licht und über synthetische Versuche an Silikatschmelzen mit eingebautem zweiwertigem Europium. *Naturwiss.*, 1939, vol. 27, p. 275. [M.A. 7 530.] Lumineszenzuntersuchungen an Feldspäten und anderen Mineralien mit seltenen Erden. *Chemie der Erde*, 1940, vol. 13, pp. 363–386. Die Bedeutung der Fluoreszenz in der Mineralogie und Petrographie. Beiträge zur Fluoreszenzmikroskopie (special volume of Mikroskopie), Wien, 1949, pp. 102–118. [M.A. 11–158.]

W. R. Foster, Useful aspects of the fluorescence of accessory-mineral-zircon. *Amer. Min.*, 1948, vol. 33, pp. 724–735. [M.A. 11–158.]

² A. F. Wilson, The charnockitic and associated rocks of north-western South Australia. Part I. The Musgrave Ranges. An introductory account. *Trans. Roy. Soc. South Australia*, 1947, vol. 71, pp. 195–211. [M.A. 10–438.]

method is tedious but useful, for the fluorescent grains may then be hand-picked more readily for optical and other tests. For routine investigation, however, the rock hand-specimens themselves are studied. They are held as close as possible to the source of ultra-violet radiation, and carefully observed. (It is advisable to view the specimen through plate glass to protect the eyes from reflected ultra-violet radiation).

The fluorescing zircons are revealed as tiny orange or yellow specks, scattered—usually quite regularly—throughout the rock. It is not difficult to prize a fluorescing crystal from the rock, to perform the simple optical tests necessary to distinguish zircon from apatite, which may display a similar fluorescence. In the writer's experience many more zircons display fluorescence than do apatites.

2. *Felspar*.—The pale-rose fluorescence of certain potash-felspars was first noticed by the writer early in 1949.¹ Detection of fluorescence is often only possible if the specimen is held very close to the source of the short-wave (2537 Å.) ultra-violet radiation, and the study made in a darkened room. Felspar (and to a lesser extent zircon) shows its best fluorescence when placed under the radiation from a set which has been in operation for at least two minutes. Erratic results may be obtained if the worker is impatient, or persists in switching off the set to study the rock in ordinary light. Moreover, if dry-cell batteries are used, care must be taken to ensure a reasonably constant voltage. Intensity of 2537 Å. in 'mineralight' diminishes greatly with a small drop in voltage, and this notably affects the response of many minerals. The writer prefers to use a freshly charged 6-volt accumulator.

III. USE OF FLUORESCENCE PHENOMENA IN THE INVESTIGATION OF SOME CENTRAL AUSTRALIAN ROCKS.

A. *Rocks from the Ayres Ranges.*

The use of fluorescent felspar and zircon may be illustrated from the results obtained in an examination of the pre-Cambrian rocks of the Kulgera Hills in the Ayres Ranges. The oldest rocks in the area are greywackes, arkoses, and quartzites. These are but little metamorphosed, and are well exposed three miles east of Kulgera Head Station. When tested under radiation of both 2537 and 3650 Å., neither fluorescent felspar nor zircon could be detected in these older rocks. In places, however, the greywackes (for example) show the beginnings of the

¹ An early observation on felspar and granite was by J. Elster and H. Geitel, *Ann. Phys. Chem. (Wiedemann)*, 1891, vol. 44, p. 733. Records for several varieties of felspar have been given by E. Engelharat, *Inaug.-Diss. Jena*, 1912, and by L. H. Borgström, *Bull. Comm. Géol. Finlande*, 1936, no. 115, p. 354. [M.A. 6-461.]

Development of porphyroblasts of feldspar. In areas of more intense feldspathization, numerous feldspathizing veins and porphyroblasts of potash-feldspar, up to 3 cm. in least dimension, were seen. This feldspar displays a notable rose-pink fluorescence under intense ultra-violet radiation of 2537 Å.

Most commonly, however, the basement rocks of the Kulgera Hills are contorted sillimanite-cordierite- or biotite-garnet-gneisses of sedimentary origin. Though carefully studied, nowhere was fluorescent feldspar (or zircon) seen in these, until there is a development of obvious 'secondary' feldspathic veins or porphyroblasts. There is no mistaking fluorescent feldspar if it is present.

Elsewhere in the area (e.g. $1\frac{1}{2}$ miles west of Top Well, Kulgera), the process of feldspathization has been so thorough that a rock of granite composition and appearance has been formed in situ. The relict contorted gneissic tendency of the old gneisses is still decipherable in the 'granite'. In this rock type, the feldspar is notably fluorescent, but no fluorescent zircon is present.

The highly feldspathized (or granitized) rocks are intruded by considerable masses of coarse to medium-grained granite. These granites have features, usually taken as field evidence of magmatism (cross-cutting characters, many with fine grained margins; uniformity of rock mass; &c.), and it is in these that a strongly fluorescing zircon is abundant. The 'magmatic' granites, then, display both fluorescent zircon and potash-feldspar.

Although fluorescent zircons did not appear until magmatic material was introduced, all igneous phases after the emplacement do not necessarily contain both fluorescent feldspar and zircon. The beryl-muscovite pegmatites, for example, contain a beautiful pink fluorescent microcline, but none of the plentiful dark zircons fluoresce. Non-fluorescent weakly radioactive zircons are plentiful in similar pegmatites, which cut the parent granodioritic igneous rocks at Ernabella in the Musgrave Ranges. The parent rock of the pegmatitic zircons contains abundant fluorescent zircons (Wilson, loc. cit., p. 208). Spectroscopic analysis of these pegmatitic zircons has shown the presence of notable Fe, Mg, Al, Th, &c., and it is probable that iron, and others of these elements, may inhibit the fluorescence in these pegmatitic zircons.

Aplitic rocks are not common, but where found, are usually so fine-grained that a study of fluorescence is difficult. However, granitic aplites of this area display neither fluorescent feldspar nor zircon, as far as can be determined.

In addition to these dike rocks, which are confined to the granite, there are considerable numbers of microgranitic dikes and small bosses throughout the gneissic terrains. Where phenocrysts of feldspar occur, these fluoresce strongly, and some fluorescent zircon is present. This confirms the field evidence that these are micro-phases of the coarse mobilized or magmatic granites.

Study has shown that the development of crush augen-gneisses, and considerably mylonitized rocks, does not affect the fluorescence of either feldspar or zircon. In the event of introduction of new material in the crush zone, the feldspars (and to a lesser extent the zircon) may, of course, become affected. This may be of great value in recognizing and mapping the original rocks of a crush zone, provided that the general characters of the major rock types have been previously determined. In the Kulgera Hills, greatly crushed 'magmatic' granites can thus be readily distinguished from greatly crushed 'granitized' (i.e. non-mobilized) granites and feldspathized gneisses, by the presence in the magmatic granites of both fluorescent feldspar and zircon, and, in the latter group, of fluorescent feldspar only.

It appears, then, that the following generalizations can be made concerning the Kulgera Hills rocks:

- (a) *The original rocks* (both little metamorphosed and relatively highly metamorphosed sediments) contain neither fluorescent feldspar nor zircon.
- (b) *Feldspathization* (with development of porphyroblasts) causes introduction of fluorescent potash-feldspar, but any zircon present is non-fluorescent.
- (c) *Granitized granites* (i.e. those formed in situ) contain abundant fluorescent potash-feldspar, but non-fluorescent zircon.
- (d) *Magmatic granites* (coarse and marginal facies) contain both fluorescent feldspar and abundant fluorescent zircon.
- (e) *Pegmatites* contain fluorescent potash-feldspar, but the fluorescence of zircon appears to be inhibited, possibly by the concentration of certain poisoning elements in the late 'liquors'.
- (f) *Intense crushing* has no appreciable effect on the fluorescence of either zircon or feldspar.

B. Rocks from the Musgrave Ranges.

In a previous paper (loc. cit., p. 201), a classification of the major rock groups was suggested on the basis of fluorescence of zircons. These earlier investigations were carried out before the presence of a fluorescent

lspar was suspected. The results, however, need little correction. A few gneisses, listed as non-fluorescent, display some poorly fluorescing zircons under the more intense short-wave ultra-violet radiation used in the more recent studies.

Certain gneisses (especially most of the group showing obvious sedimentary characters) contain a non-fluorescent zircon. This is usually of pale-fawn colour, and more murky in appearance than the clear colourless fluorescent zircons of the same area (loc. cit., p. 203). Other gneisses (usually those showing a more intense feldspathization) contain a small number of fluorescent zircons.

The main intrusive rock of the eastern Musgrave Ranges, the medium-grained charnockitic granodiorite of Ernabella, which intrudes all types of gneissic and granulitic charnockite, always contains an abundance of prismatic fluorescent zircons. This acidic intrusion is widespread. In its central part, near Ernabella, the importance of hypersthene and diopsidic augite, and paucity of hornblende and biotite, and other 'wet' minerals, is evident under the microscope (loc. cit., p. 206). This facies of the intrusion, though displaying abundant fluorescent zircon, contains a non-fluorescent potash-felspar (when tested under different intensities of both 2537 and 3650 Å.). In portions of the same 'batholith', and in certain 'cupola' facies, hornblende and biotite are present, instead of hypersthene and diopsidic augite, and twinned microcline takes the place of orthoclase or untwinned microcline.

A decrease, towards the east, of the pressure-temperature conditions prevailing at the time of crystallization, has enabled an increasing development of these 'wet' minerals from the Central Musgrave Ranges eastward, for one hundred miles, to the Kulgera Hills, and the attendant potash-felspar displays an increasingly intense pink fluorescence.

The following five examples¹ illustrate this gradation:

- i. *Ernabella* charnockitic granites and granodiorites contain plentiful hypersthene, diopsidic augite, and non-fluorescent orthoclase or poorly twinned microcline.
- ii. *Bald Hill*—a coarse facies developed in a small cupola, 14 miles N.E. of Ernabella, and containing plentiful hornblende and biotite, but no pyroxenes. Strongly fluorescent microcline is present.
- iii. *Sentinel Hill*—a large granitic mass representing an 'island' of igneous rock, which crystallized under pressure-temperature conditions

¹ Fluorescent zircon appears in all non-pegmatitic and non-aplitic facies of this intrusion, and is apparently not affected by the crystallization conditions to the same degree as is felspar.

only a little lower than those obtaining at Ernabella, which is 25 miles to the WSW. Hypersthene and diopsidic augite, as well as hornblende and biotite, are well represented. The feldspar is a moderately pink fluorescent microcline.

iv. *Beefwood Creek Hills* (about 50 miles ENE. of Ernabella)—the granites contain somewhat pinker potash-feldspars, as seen in hand-specimen, and hornblende, diopsidic augite, and biotite are well developed. There is a notable fluorescence of well-twinned microcline.

v. *Kulgera Hills* (part of Ayres Ranges, 100 miles ENE. of Ernabella).—The granites are similar to those of the Beefwood Creek Hills, but contain hornblende and biotite, and rarely any pyroxene. A strongly fluorescent, coarsely cross-hatched microcline is present.

A similar relation between the pressure-temperature conditions, and the intensity of fluorescence in the potash-feldspars, appears to hold in the case of the granulites and gneisses. The hypersthene-granulite facies contains a non-fluorescent orthoclase (or poorly twinned microcline), whereas comparable rocks (of the same great system of metasediments) of the hornblende-gneisses, and biotite-gneisses, and associated migmatites, display, in the main, a fluorescent potash-feldspar (usually a well-twinned microcline).

vi. *Upsan Downs granites* (25 miles WSW. of Ernabella).—These are flesh-coloured porphyritic foliated granites, similar in many respects to those of the Everard Ranges, which lie some 70 miles to the SE., across a desert destitute of rock outcrops. The potash-feldspar of both granite and surrounding feldspathized gneiss is notably fluorescent, but only in the mobilized granites is a fluorescent zircon present.¹ This strengthens the writer's suggested correlation of these rocks with the Everard Range porphyritic granites.

vii. *The Mt. Woodroffe-Trudinger Pass intermediate and basic rocks*.—The andesine of this great sill-like structure (loc. cit., p. 205) fluoresces a pale but distinct pink under intense 2537 Å. radiation. No fluorescent zircon is present.

viii. The *Plagioclase* of the *Basic residual lenses* in the feldspathized gneisses often displays a pale but distinct pink fluorescence, but only under intense 2537 Å. radiation.

ix. Some *pegmatite plagioclases* (mainly albite) of the Sentinel Hill area and Kulgera Hills are notably activated.

¹ In the earlier paper (p. 206) it was stated that these rocks contained a non-fluorescent zircon. Under the more intense 2537 Å. radiation now in use, the zircon is activated.

The significance of the comparable fluorescence of both plagioclase and potash-felspar is as yet unknown. Since the two mineral species have a similar structure, it is conceivable that the one activator could give a similar fluorescence in both minerals. It is suggested, however, that the activator (? rubidium or caesium) is associated with the potash-felspar phase in the exsolution antiperthites of these rocks. This could account for the relatively weak fluorescence of certain plagioclases in the gneisses and granulites, when compared with that of the potash-rich felspars.

IV. SOME OTHER EXAMPLES OF FLUORESCENCE PHENOMENA.

A. *South Australia*.—Strongly fluorescing microclines are a feature of the Murray Bridge and Goonalpyn fluorine-rich granites, and of the Minnipa-Wudinna granites on Eyre Peninsula. There are several other important granites and feldspathized gneisses. In addition, apatite, fluorescing in orange, is important in many Boolcoommatta and Mt. Painter granites, as well as the pegmatites of the eastern Mt. Lofty Ranges.

B. *Other Australian States*.—From a study of over one thousand museum specimens, it appears that in each State several granitic areas occur in which fluorescence of felspars is a feature. There are other granites which display no fluorescence. It is suggested, therefore, that critical work on carefully collected material should prove of considerable petrological value in any of the Australian States.

C. *European and American* granitic specimens were studied with similar results. Examples with notable fluorescent felspar are Shap Fell, England; Peterhead, Scotland; most of those of the Odenwald, Germany; &c. Some of those displaying no fluorescence are many Cornish granites; Ramberg, Harz Mts., &c.

V. CONCLUSIONS.

It is apparent that the pink fluorescence of the potash-felspars is a widespread phenomenon, as also is the orange fluorescence of both apatite and zircon. Nevertheless, there are sufficient rocks, which do not display any fluorescence, to make a study under ultra-violet radiation a valuable aid in petrological research. Since, however, the indiscriminate use of fluorescence can lead to misleading results, the following principles should be understood, before the phenomenon is used for this purpose:

1. Fluorescence is often due to a trace element (or elements) which

appears to distort the structure of a mineral. This substance, the activator, can be detected only with great difficulty, even spectroscopically, in natural substances.

2. Too much of the activator can 'quench' any fluorescence.

3. The presence of other elements (e.g. iron) may act as 'poisons' and thus inhibit fluorescence. The application of these principles is seen when a mineral (e.g. zircon), which is normally fluorescent in a certain area is non-fluorescent in some associated pegmatites. The mineral has presumably picked up from the pegmatitic 'liquors' certain 'poisoning' elements, so common in such an environment. It is, therefore, unwise to attempt a correlation of pegmatites by fluorescence alone.

4. The petrological use of fluorescence is most significant in the examination of rocks of pre-Cambrian or early Palaeozoic areas. The basement rocks of such terrains often contain no fluorescent minerals. In younger rocks second (or later) generation fluorescent minerals may be found, and the phenomenon may be very confusing. It is important, therefore, to spend time in a preliminary study of the oldest rocks of an area before attempting to make use of fluorescence correlations.

5. The conditions under which crystallization is effected may have a considerable bearing on fluorescence. In a major intrusion deep-seated areas may show features different from the cupola or marginal facies (e.g. Musgrave Ranges, Central Australia). This may be due to the inability of the activators (even if present) to enter into the structure under the high pressures and temperatures prevailing at the place of crystallization. Felspars seem to be more sensitive than zircons or apatites in this respect. Empirically, there appears to be a relation between the intensity of feldspar fluorescence and the coarseness of the twinning in microcline. The variability of the cross-hatched twinning may be due to varying amounts of activator ions (and possibly other trace elements) in the feldspar structure. Some of these, by virtue of their ionic volume, may have facilitated the development of a coarsely cross-hatched twinning, either on the inversion of a pre-existing orthoclase, or in a primary microcline. In most pegmatites the pressure-temperature control is such that more of the abundant volatiles and trace elements is able to be incorporated into the complex structures. Many of these ions, however, may be in excess of the minute quantities required to give the optimum fluorescence, and others may act as 'poisons'.

6. The above factors indicate that only those rocks which show similar pressure-temperature conditions and similar composition should

be compared by fluorescence of minerals. For instance, granitic aplites should not be compared with charnockitic granites, nor biotite-microcline-granite with hypersthene-orthoclase-granite, nor even similar facies granites and gabbros.

It is considered that if fluorescent data be carefully assembled in connexion with each petrological problem, not only will much of immediate value be derived, but the increasing world-wide accumulation of facts will allow more accurate deductions and correlations to be made.

Acknowledgements.—The research recorded in this paper was carried out in the Department of Geology, University of Adelaide. The field-work was made possible by a Commonwealth Research Grant, administered by that University. Professor Sir Douglas Mawson, Messrs. A. W. Kleeman, and H. Brock of Adelaide, and Professor R. T. Prider of the University of Western Australia, have read the manuscript and made useful suggestions.

Pseudomorphs of pyrrhotine after pyrite in the Ballachulish slates.

By HENRICH NEUMANN, Dr. Philos. (Oslo)

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[Taken as read, June 8, 1950.]

THE Ballachulish slates,¹ exposed to the north and south of Loch Leven in Argyllshire, contain, in most places, cubes of pyrite up to half an inch in diameter. During a visit to the area in the spring of 1949 the writer's attention was attracted by the dark colour of the 'pyrite' cubes in the North Ballachulish slate quarry a little more than a mile east of Onich. On examination these proved to consist of a mass of haphazardly orientated crystals of pyrrhotine with irregular outlines. Slates collected from the main working quarry on the south shore of Loch Leven, on the other hand, contain cubes which are single crystals of unaltered pyrite.

This feature appeared to merit further investigation and in June 1949 the area² was revisited in order to ascertain the distribution of pyrite and pyrrhotine in relation to the geology of the region. As shown in fig. 1 the pyrite crystals are altered to pyrrhotine in a zone around the Ballachulish granite, while at greater distances from the contact the pyrite is unaltered. An intermediate zone can be recognized in which the pyrite crystals are either *partly* altered to pyrrhotine, or pseudomorphs of pyrrhotine after pyrite, and unaltered pyrite occur together in the same specimen. It is clear from this distribution that the pyrrhotine must have been formed by contact metamorphism of pre-existing pyrite in the slates. This is by no means an unusual phenomenon as the occurrence of pyrrhotine as a contact-metamorphic product of pyrite is known from a great number of other localities.³

¹ For a further description of the Ballachulish slates see: Memoir of the Geological Survey, Scotland, no. 53, The Geology of Ben Nevis and Glen Coe (1916).

² During the field-work I was accompanied by O. v. Knorring, fil. lic., to whom thanks are due for help and discussions of the problems dealt with in this paper.

³ It was originally thought that the existence of pyrrhotine might be dependent on the varying degree of regional metamorphism of the slates, and that the distribution of pyrite and pyrrhotine might give further clues to the tectonical architecture of the area. There is no evidence whatever for such an assumption. I am indebted to Professor W. Q. Kennedy for numerous discussions of the geology of the surroundings of Loch Leven, and for the keen interest he has taken in these investigations.

The alteration of pyrite to pyrrhotine is a very simple chemical process as follows: $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$. The sulphur formed by the dissociation of pyrite is probably reduced to sulphide ions or oxidized to sulphate ions and then removed as such from the place of formation.



FIG. 1. Distribution of pyrite and pyrrhotine around the Ballachulish granite. Open circles indicate pyrite, filled circles pyrrhotine, and half-filled circles pyrite and pyrrhotine together. Crossed is Ballachulish granite, stippled the contact-metamorphic aureole according to Memoir of the Geological Survey, Scotland, no. 53.

The temperature at which this process has taken place is not easy to assess with any degree of accuracy. At atmospheric pressure pyrite dissociates to pyrrhotine and sulphur vapour at a temperature of 900°C . At this temperature the sulphur vapour-pressure of pyrrhotine is 1 atm. and decreases rapidly with decreasing temperature.¹ At 600°C . it is less than 20 mm., and will be very small indeed at 500°C . Above 690°C . no experiments have been carried out to determine the sulphur vapour-pressure of pyrite, but the shape of the vapour-pressure

¹ R. Juza and W. Biltz, Zeits. Anorg. Chem., 1932, vol. 205, p. 273. [M.A. 138.]

curve indicates that it will increase very rapidly with increasing temperature.

The pressure on the pyrite cubes at the time of alteration was undoubtedly considerable, on account of the overlying rocks, and if the slates were impenetrable to sulphur vapour, it could be concluded that the pyrrhotine pseudomorphs were formed at a temperature considerably higher than 690°C . However, the sulphur vapour has probably been removed to some extent, either as such or by oxidation to SO_4^{2-} or reduction to S^{2-} . Either possibility means a transport of material to or from the site of reaction, and it can safely be assumed that a certain sulphur vapour-pressure must have been maintained around the pyrite cubes. Even if the most generous allowances are made for a removal of sulphur it seems highly improbable that the formation of pyrrhotine can have taken place at a temperature lower than $500\text{--}600^{\circ}\text{C}$. The curve of dissociation pressures of pyrite worked out in the Geophysical Laboratory¹ fully confirms this assumption.

These considerations throw an interesting sidelight on the genetical problems of the Ballachulish granite. Pyrrhotine is formed up to $1\frac{1}{2}$ miles from the granite contact, which is considered to be nearly vertical. The temperature within the granite itself—whatever its mode of formation—must have been higher than in the surrounding rocks. It seems reasonable to assume a difference of at least 100°C . over a distance as great as $1\frac{1}{2}$ miles. We are, therefore, led to postulate that the Ballachulish granite must have been formed at a temperature not lower than $600\text{--}700^{\circ}\text{C}$., a temperature of formation which might be expected in the case of a granite formed by solidification of a granitic magma.

It has long been recognized that nickel tends to be enriched in pyrrhotine and cobalt in pyrite. This is very clearly illustrated in the nickel deposit at Flåt in southern Norway.² The ore consists of pyrite, pyrrhotine, pentlandite, and chalcopyrite deposited in the order in which they are mentioned. The pyrite from Flåt contains 0.78 % Co (average of 13, ranging from 0.47–1.00 % Co) and less than 0.01 % Ni, giving a ratio Ni/Co less than 0.013 for pyrite, while the ratio Ni/Co for pyrrhotine from the same deposit is about 80. The Ni/Co ratio is, therefore, about 8000 times larger for pyrrhotine than for pyrite.

It is a matter of interest, therefore, to examine the behaviour of the Ni and Co content of the pyrite crystals in the Ballachulish slate during

¹ H. E. Merwin and R. H. Lombard, *Econ. Geol.*, 1937, vol. 32, p. 222. [M.A. 7-143.]

² H. Bjørlykke, Flåt nickel mine. *Norges Geol. Undersøk.*, 1947, no. 168b. [M.A. 10-228.]

the alteration to pyrrhotine. Several determinations of Ni and Co have been carried out¹ and results are shown in table I. The Ni and Co contents

TABLE I. Nickel and cobalt contents in pyrites and pyrrhotines from the following localities: I, easternmost of two slate quarries, west of West Laroeh; II and III, western part of North Ballachulish slate quarry; IV, easternmost of three old slate quarries, SE. of Laroeh; V, big slate quarry, Ballachulish (now worked); VI, easternmost of two slate quarries, west of West Laroeh.

	% Ni by wt.	% Co by wt.	Ni atoms per 10,000 Fe atoms.	Co atoms per 10,000 Fe atoms.	Ni/Co atomic (& mean).
Pyrrhotine I	0.076	0.042	11.70	6.47	1.81
„ II	0.012	0.014	1.84	2.08	0.88
„ III	0.015	0.010	2.35	1.58	1.49
Pyrite IV	0.012	0.033	2.47	6.63	0.37
„ V	0.005	0.019	0.95	3.79	0.25
Pyrrhotine VI	0.013	0.022	2.00	3.41	0.59
Pyrite VI	0.013	0.027	2.66	5.50	0.48

of the pure pyrites and pyrrhotines from localities I-V clearly demonstrate that there is a systematic difference in the Ni/Co ratios for the two minerals. This difference can originate in one of two ways: (1) either by a decrease of the Co content during the alteration, or (2) by an increase of the Ni content. The first alternative seems the more probable, but the variation of the content of Ni and Co in the different crystals which have been analysed is too great to justify a definite conclusion. An analysis of the pyrite and pyrrhotine from a single, partly altered cube appeared to be the only method whereby the problem could be solved. A specimen from the easternmost of two slate quarries, west of West Laroeh, contained a reasonably sized cube of pyrite partly altered to pyrrhotine. This crystal was crushed, and the pyrrhotine removed from the pyrite with a magnet. Because of the intimate intergrowth between the two minerals it was impossible to obtain pure samples. The pyrrhotine sample contained some pyrite and vice versa. The analyses of the impure samples (table I, pyrrhotine VI and pyrite VI) show, nevertheless, that the cobalt content has a pronounced tendency to decrease during the alteration of pyrite to pyrrhotine, whereas the nickel content remains nearly constant. It would appear, therefore, that when the Fe atoms in the pyrite lattice rearranged themselves to form a pyrrhotine lattice, any unsuitable atoms tend to be rejected.

¹ The determinations were done by optical spectrographical methods, using the iron in pyrite and pyrrhotine as comparison substance. The intensities of the following lines were compared: Co 3453.5-Fe 3451.9 Å.; Ni 3050.8-Fe 3053.4 Å. The spectrographical work was done by L. Lund, mag. scient., and I offer my sincere thanks for his help and assistance.

Cobalt apparently does not fit the pyrrhotine lattice as well as does nickel, and has consequently been rejected more easily. The result is seen in the pronounced drop in the Ni/Co ratio demonstrated by the analyses given above.

A general rule may be formulated to the effect that when one mineral replaces another it does not, without modification, inherit the trace elements of the older mineral, but tends to readjust the trace-element content according to the properties of its own crystal lattice.

Thermal study of some manganese oxide minerals.

By J. LAURENCE KULP and JOSE N. PERFETTI.

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[Communicated by Prof. P. F. Kerr; taken as read June 8, 1950.]

Introduction.

IN the past decade, differential thermal analysis has developed into a very useful mineralogical technique. The theoretical background of this method has been treated by Speil, Berkelhamer, Pask, and Davies (1945) and has been modified by Kerr and Kulp (1948, 1949). The application of the method to the clay minerals has been carried out with considerable success by a number of workers in Europe and America. In particular, Grim and co-workers (1942, 1947, 1948) have produced a number of significant papers dealing with the thermal analysis of clays. The method has been extended to other mineral groups such as the carbonates (Faust, 1949; Beck, 1946; Kerr and Kulp, 1947; Luthbert and Rowland, 1947; Kulp, Kent, and Kerr, 1950), phosphates (Manly, 1950), sulphates (Kulp and Adler, 1950), quartz (Faust, 1948), and the hydrous iron oxides (Kulp and Trites, 1950).

Since differential thermal analysis provides both qualitative and quantitative data of the presence of thermally active minerals, it is ideally suited to a study of fine-grained natural aggregates which present a difficult problem to other methods of attack. It appeared that the natural occurrence and importance of the manganese oxide minerals would make a preliminary investigation by thermal analysis desirable. The publication of two papers on the mineralogy of the manganese oxides (Fleischer and Richmond, 1943; and Gruner, 1943) has assisted greatly in understanding the complexities of the group, but no thermal analysis was carried out in these investigations. In this study it has been the objective to define the thermal curves of the simpler manganese minerals and to show how the method may be applied to natural mixtures.

The authors wish to acknowledge the advice and encouragement of Prof. Paul F. Kerr. Prof. Ralph J. Holmes made some very helpful suggestions on the X-ray diffraction technique used. Dr. Georges Pardo acted as interpreter and contributed several valuable ideas on the elaboration of the text. Miss P. K. Hamilton and Dr. H. D. Holland

assisted in taking some of the thermal curves. Dr. H. H. Adler obtained the curve on ramsdellite in the course of another study.

Method.

Under the application of heat substances undergo exothermic and endothermic changes. This application may be carried out dynamically (differential thermal analysis) in which the system is heated at a constant rate. It is called *differential* because the temperature difference between an inert material and the sample is measured as both are being heated at a constant rate.

In order to obtain a satisfactory curve it is necessary to control the rate of heating so that it is uniform and reproducible, to measure the temperature with reasonable precision ($2-5^{\circ}\text{C.}$), and to record the slight differences in temperature caused by changes in the sample as the temperature is raised. The last is determined by the use of a two-headed thermocouple, one head of which is placed in the sample while the other is placed in an inert material (generally alundum). The connexions are so arranged that the potentials oppose each other. Hence, if there is no reaction in the sample, the potentials balance and there is no net heat flow. Any heat effect in the sample will cause an unbalance and this is picked up on a sensitive recording device. The practical result is a plot which is a straight line when no reaction is taking place, but shows deviations in one direction or the other depending on the nature of the heat effect.

Since it is unlikely that any two minerals have chemical bonds of identical strength, they will decompose, oxidize, or change phase at different temperatures. The temperature at which a peak occurs often indicates which mineral is present. Since many minerals undergo several endothermic or exothermic changes in the temperature range studied, the aggregate peaks at the proper temperatures suffice in many instances to identify the mineral. The relative amplitude and shape of a peak is a function of the type of change, as well as the rate at which it occurs. The amplitude of the peak is related to the concentration of a particular mineral, and hence semi-quantitative estimates are possible by simple inspection. The area under the peak is proportional to the concentration according to the theoretical treatment of the problem.

Since each mineral will ordinarily yield a characteristic set of peaks independent of the foreign constituents, frequently the members of a mixture in a fine-grained aggregate may be defined. Obviously the more complex the mixture and the larger the number of components with

overlapping peaks the more difficult becomes the interpretation. Usually, however, X-ray, petrographic, and thermal data together are adequate to define the major minerals present in a mixture if the group is thermally reactive. In order to obtain quantitative results, it is necessary to prepare comparison curves by diluting pure minerals with some inert materials similar to those in the naturally occurring aggregates. A calibration curve based upon the amplitude of a significant peak is then constructed. The amplitude of the mineral peak in an unknown then yields by comparison the appropriate percentage of the mineral in the unknown. The amplitude is a more convenient measurement than the area under the peak and except for very sharp peaks is reproducible within the limits of experimental error.

Apparatus and procedure.

The apparatus used in this investigation is described by Kerr and Gulp (1948). The most recent modification is shown in fig. 1. It consists of four major components: a vertically mounted, wire-wound electrical resistance furnace; the specimen holder block and necessary attachments; the programme controller for automatically maintaining a constant rate of heating; and a Leeds and Northrup Speedomax electronic recorder with a full scale of 3 millivolts. Recent improvements include changing the recorder from a 6- to a 16-point type, 4 points of which are on absolute temperature while the other 12 are on differential temperature. A direct current electronic pre-amplifier coupled with an automatic synchronized rotary switch makes it possible to obtain sensitivities equal to any galvanometer without the attendant inconvenience and inefficiency of photographic recording.

The mineral specimen is ground to pass 80 mesh and packed into the specimen-holder recess to finger tightness. This procedure permits reproduction of peak amplitudes within the limits of experimental error. Experimentation indicates that processes such as weighing the sample, obtaining a narrow particle-size range, and bringing to constant humidity are unnecessary for most routine work. For special experiments any or all of these factors may require control.

Where quantitative calibration curves are desired, the mixture of the known materials should be prepared to correspond in particle size and intimacy with the natural unknown material. However, in most cases, rough mixture by weight gives the desired result.

All of the amplitudes are strictly comparable since they are corrected to an arbitrary reference curve of standard Georgia kaolinite. The

temperature range used for these studies was 100–1050° C. The heating rate was 12½° per minute and the thermocouples were chromel-alumel.

The samples used were essentially homogeneous. Gangue observable by microscopic observation was rejected. Transparent impurities were identified in so far as possible by study of the powder with a petrographic

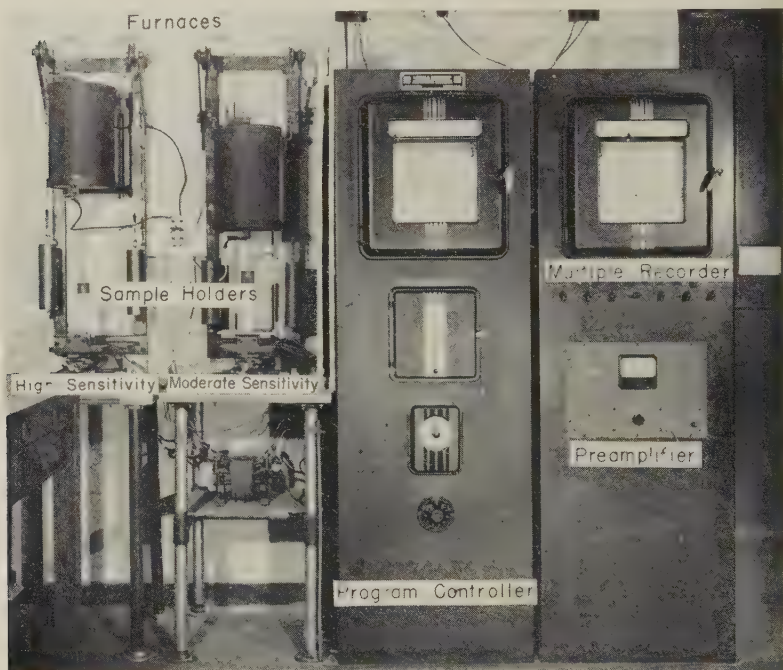


FIG. 1. Differential thermal apparatus at Columbia University.

microscope. Artificial mixtures were prepared from mineral specimens which had been carefully checked for purity by X-ray diffraction, thermal analysis, and petrographic examination.

Debye X-ray powder patterns were obtained on most of the specimens by the use of iron radiation. Patterns of the material heated to temperatures above that of the thermal curve peaks were also obtained so that the resultant phase could be identified.

Typical thermal curves.

Pyrolusite and ramsdellite.—A number of specimens that appear to be high quality pyrolusite were thermally analysed. The results appear

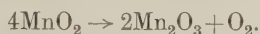
in fig. 2. The typical thermal curve for this mineral shows a major endothermic peak between 670 and 700° C. and a second lesser peak 1000–1010° C. The initial break occurs between 580 and 670° C.

The curve is slightly asymmetrical with a steeper return slope. All of these specimens showed a characteristic pyrolusite X-ray diffraction pattern with no extra lines. A sample (2–9) of the Numadate mine heated to 850° C. gave a distinct pattern similar to bixbyite ($\text{Mn,Fe}_2\text{O}_3$).

The data of the heated pyrolusite are given below for the three principal lines and compared with the American Society of Testing Materials Index of X-ray patterns.

	(1)	(2)	(3)
Mn_2O_3	2.68	1.66	1.42
Bixbyite	2.73	1.65	1.41
Pyrolusite heated to 850° C. .	2.69	1.67	1.43

It has been shown that bixbyite has the same crystal structure as In_2O_3 (Pauling and Shappell, 1930), hence the product of the 700° C. peak in pyrolusite is due to the endothermic reaction



The same specimen heated to 1010° C. gave the pattern of hausmannite. Similar results were obtained with the specimens from Coburg (2–4) and Penny Cape (2–6).

There are several minor differences in these curves (fig. 2) which are of interest. It is also noteworthy that the water content of these specimens is very low and that most of it is released before 100° C. This is consistent with the coarsely crystalline appearance of these specimens. All specimens except Tabua (2–2) were coarsely fibrous or platy and bright. The Tabua specimen consisted of very uniform fibres with traces of limonitic material. The minor peak at 350° C. is probably due to a few per cent. of goethite. The slight variation in the peak temperatures and amplitude are probably to be attributed to crystallite size. The low temperature (970° C.) of the Mn_2O_3 –hausmannite conversion in the Numadate mine (2–9) specimen is not entirely understood.

Fig. 3 shows two curves of pyrolusite. The specimen from France (3–1) contains some inert impurity, probably hausmannite.

The specimen of pure ramsdellite (MnO_2) from the Idorado mine (3–3) is typical. A small amount of capillary water is indicated by the slight endothermic peak at 120° C. The exothermic phase change from ramsdellite to pyrolusite is shown at 500° C. on the differential thermal curve. Subsequent to this reaction the curve is similar to that of pyrolusite as would be expected. Note that in this case as in (2–9) the final

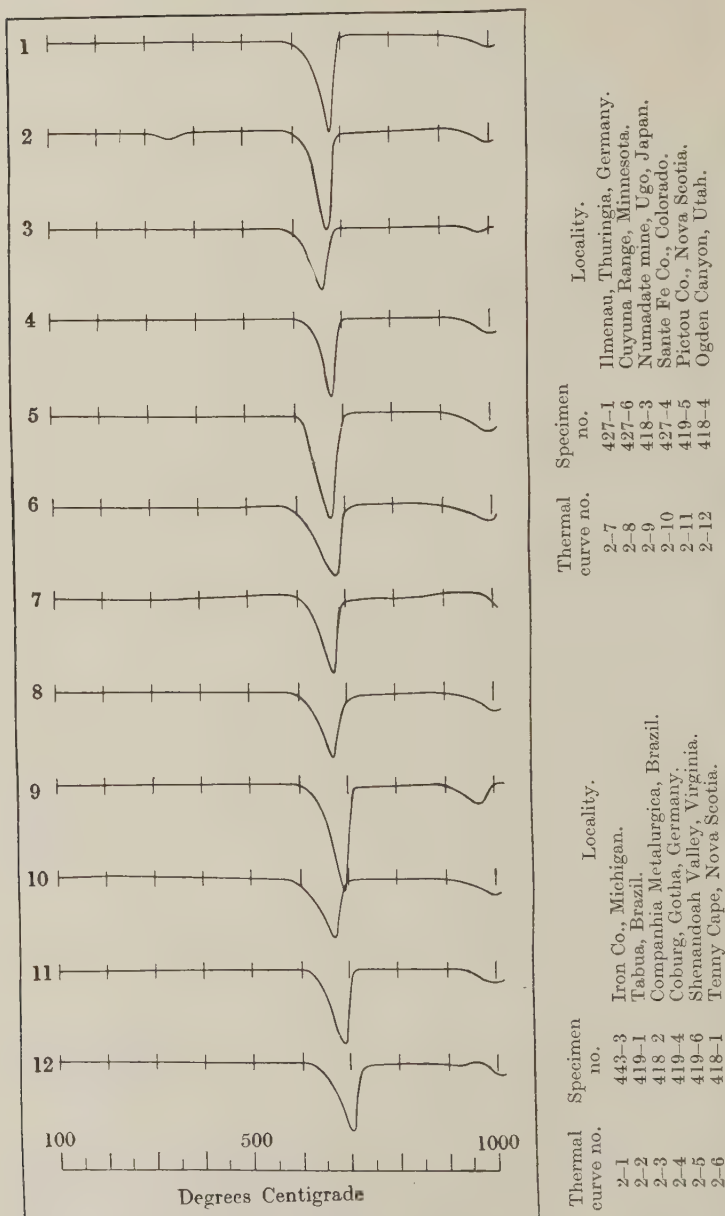


FIG. 2. Thermal curves of representative pyrolusite specimens. All specimens yielded a typical pyrolusite X-ray diffraction pattern without extraneous lines.

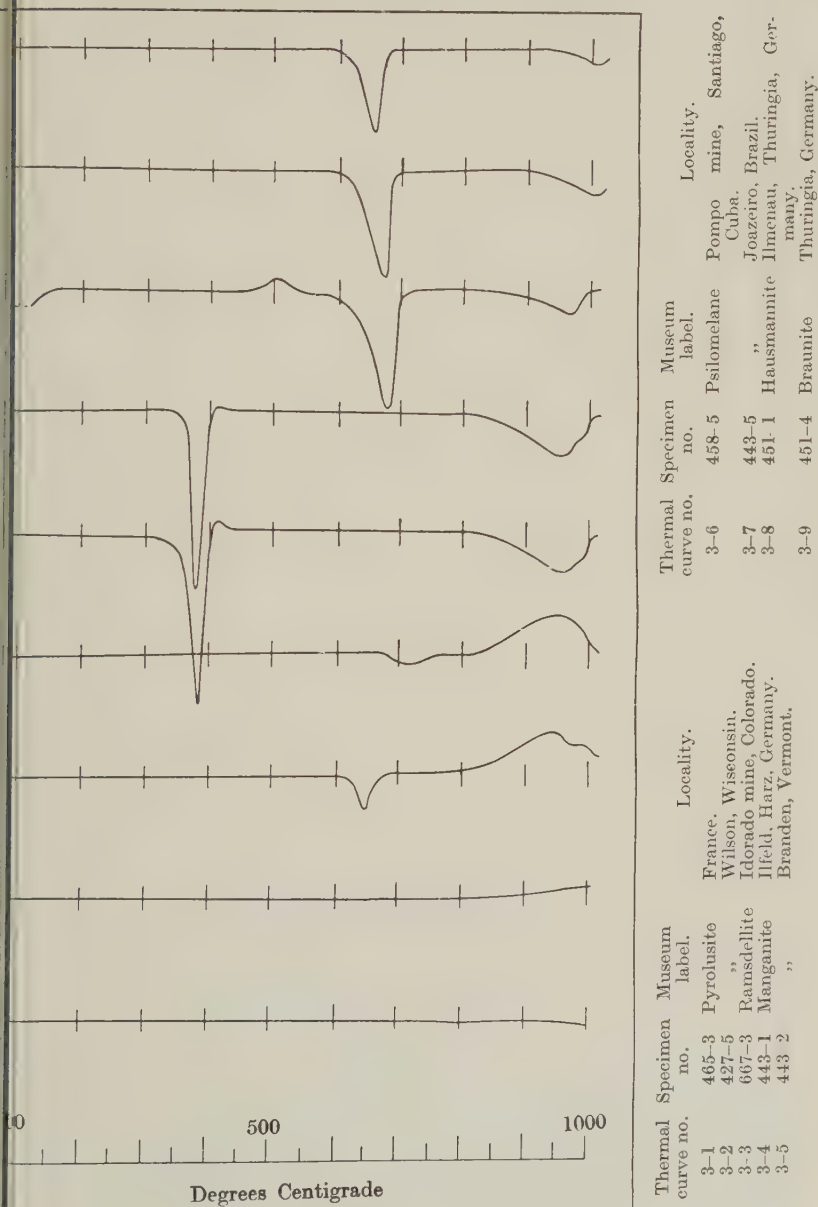


FIG. 3. Thermal curves of various manganese oxides.

endothermic peak temperature is reduced. This is probably to be related to the Mn_2O_3 crystallite size which forms in the pyrolusite decomposition. X-ray diffraction patterns taken at room-temperature (ramsdellite), 200°C . (ramsdellite), 550°C . (pyrolusite), 800°C . (Mn_2O_3), and 1000°C . (hausmannite) are consistent with the above interpretation.

Manganite.—The manganite specimens (3-4 and 3-5) show typical X-ray diffraction patterns with no extra lines. The specimens were shiny black prismatic crystals. The thermal curves show a sharp endothermic peak at 380°C . followed by a broader endothermic peak at 950°C .

The manganite goes over to Mn_2O_3 at $350\text{--}400^\circ\text{C}$. which remains stable until about 800°C . The Mn_2O_3 is less perfectly crystallized from this low temperature of formation (400°C .) as compared to the Mn_2O_3 produced from the pyrolusite decomposition at 700°C . This explains the lower temperature at which the final recrystallization starts. The slight doublet near 980°C . is not clearly understood. An X-ray pattern taken after heating to 900°C . showed only Mn_2O_3 lines, but one taken after heating to 1000°C . showed only hausmannite.

Psilomelane type.—Curves 3-6 and 3-7 of fig. 3 show the thermal curves of two specimens of the psilomelane type. The absence of analytical chemical data made it useless to study the complex members of this group. The broad exothermic reaction from 800 to 1000°C . appears typical of this group. The reaction is probably a recrystallization type of reaction. There appears to be no low-temperature reaction of this mineral. Specimen 3-7 contains about 20 % pyrolusite and gives expected inflections at 650° and 970°C . The presence of pyrolusite in this specimen was confirmed by X-ray diffraction.

Hausmannite and braunite.—One specimen of each of these high-temperature minerals was thermally analysed after X-ray diffraction examination had proved them to be monomineralic. They show no thermal reaction in the temperature range studied. This was confirmed by X-raying the specimen after heating to 1000°C .

Thermal curves of artificial mixtures.

The analysis of the mineral composition of natural aggregates of manganese oxide minerals requires a previous knowledge of the size and shape of characteristic peaks as a function of concentration. To this end a series of artificial mixtures were prepared and thermally analysed. Fig. 4 shows the results for mixtures of pyrolusite, manganite, and quartz. Note the additive effect of the high-temperature endothermic peaks of pyrolusite and manganite. Fig. 5 shows the curves for mixtures of

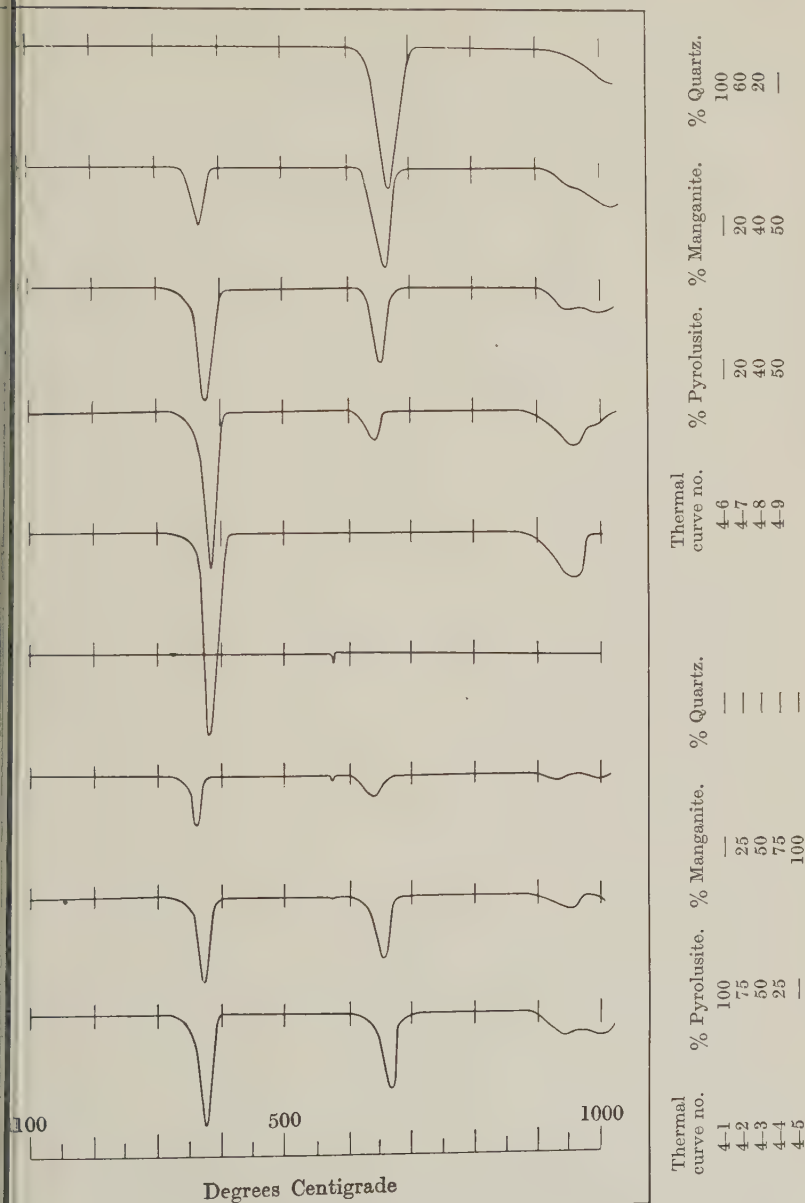


Fig. 4. Thermal analysis of artificial mixtures of pyrolusite, manganite, and quartz.

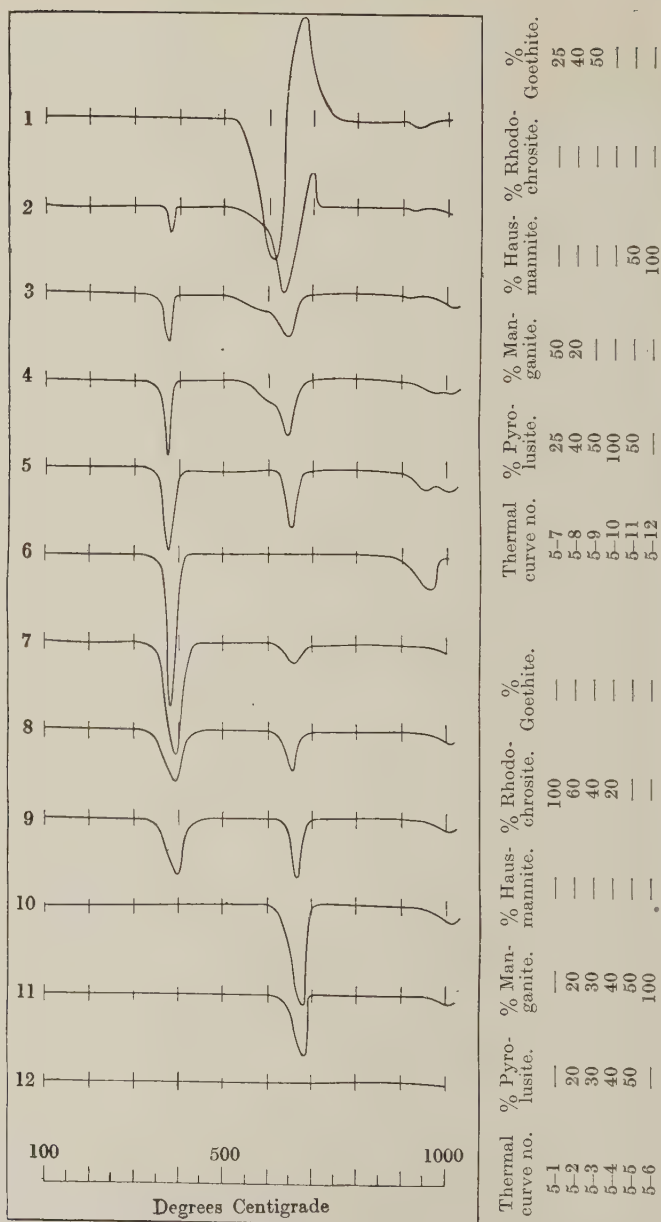


FIG. 5. Thermal analysis of artificial mixtures of pyrolusite, manganite, hausmannite, and rhodochrosite.

pyrolusite, manganite, hausmannite, rhodochrosite, and goethite. Note the broadening of the manganite peak in the presence of goethite. In general, the variation of peak amplitude or peak area with concentration is well established. These curves are used as a basis of estimating percentages of these minerals in unknown assemblages.

Representative natural aggregates.

Fig. 6 shows the differential thermal curves of fifteen natural manganese oxide aggregates. The names for the specimens as given on the museum labels are included in the accompanying table. The present results show that in several cases they had been incorrectly determined.

(6-1) labelled pyrolusite from Thuringia contains 30 % manganite, 50 % pyrolusite, and 10 % (?) psilomelane type mineral in addition to inert material which includes hausmannite; X-ray diffraction showed lines of pyrolusite, manganite, and hausmannite. (6-2) contains 40 % manganite, 10 % dusty pyrolusite, and some hausmannite. (6-3) contains 15 % manganite and goethite (?), and 10 % pyrolusite; X-ray diffraction showed only hausmannite lines. (6-4) contains 50 % quartz and 20 % pyrolusite; X-ray diffraction showed only quartz and pyrolusite lines. (6-5) shows 80 % pyrolusite with a thermally active but unidentified material giving a small sharp endothermic peak at 630° C. (6-6) contains 80-90 % lepidocrocite with possibly 10 % psilomelane type. (6-7) shows 2-6 % pyrolusite; X-ray pattern showed hausmannite lines. (6-8) contains 30 % fine pyrolusite; the specimen shows strong X-ray lines of hausmannite. (6-9) contains 25 % fine pyrolusite as well as hausmannite. (6-10) shows 20 % fine manganite and goethite (?), 10 % coarse pyrolusite, and 40 % (?) psilomelane type. (6-11) shows the presence of colloidal water and a small amount of organic matter which yields the exothermic peak at 210° C. It also contains 10 % coarse pyrolusite and possibly 10 % psilomelane. (6-12) contains hausmannite (X-ray) and pyrolusite 15 %. (6-13) is a specimen of high manganite (80 %) with the presence of some unidentified but thermally active constituent which produces the broad peak at 500-600° C. (6-14) shows the presence of some organic matter by the exothermic dome at 300-400° C., psilomelane type 80 % (?), and fine pyrolusite 10 %. (6-15) shows a thermal peak of fine calcite and gives an X-ray pattern showing braunite as the major constituent.

Conclusions.

Representative specimens of the more common manganese oxide minerals have been thermally analysed. Pyrolusite, manganite,

omssdellite, and the psilomelane type minerals give distinctive thermal reactions which may be used in the semi-quantitative analysis of the components of a natural mixture. A group of natural aggregates have been analysed and the concentrations of the various minerals, interpreted in terms of the thermal curves of artificial mixtures. The application of thermal analysis to this group of minerals provides valuable information unavailable by other standard methods of technique.

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Note on garnet crystals from Cairnie, Aberdeenshire.

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[Read June 8, 1950.]

IN 1938 large crystals of almandine garnet were collected by the writer from a cutting excavated during road-widening operations, on the main Huntly-Keith road, near Cairnie church, about $4\frac{1}{2}$ miles from Huntly. In view of their exceptional size and excellent crystal form, it is felt that the occurrence is worth recording. Garnet crystals of comparable size have been recorded by Heddle¹ from several localities. The Cairnie crystals, considering their size and excellent form, must rank with the finest recorded from Scotland.

The rocks at this cutting are coarsely banded garnet-biotite-sillimanite-gneisses with abundant quartz, oligoclase, orthoclase, and biotite, subordinate muscovite, and accessory magnetite, apatite, and zircon. Sillimanite is sporadic in occurrence, forming elongated colourless prisms up to 2 mm. across. The biotite-rich bands generally contain only small garnets, if any, but garnet is very abundant in bands rich in quartz and feldspars, and often forms a large part of the rock.

The garnets are wine-red to purplish-red in colour, and show the forms (110) and (211). The dodecahedron is usually the dominant form, and shows oscillatory combination with (211), giving a series of stepped faces. Where the two forms are nearly equally developed, the crystals appear almost spherical, due to this oscillatory combination. A great many of the crystals are about $\frac{1}{2}$ inch across, but several exceptionally large crystals, up to 2 inches across, of almost perfect proportions, have been found. For example, one dodecahedron found by the writer measures 1.88 inches along all three axial directions. Larger crystals have been found, but are more irregular, and are generally made up of various units in parallel growth.

A chemical analysis of a purplish garnet from this locality was made by the writer and is given below. The analysed material was carefully purified by hand-picking and centrifuging with heavy liquids.

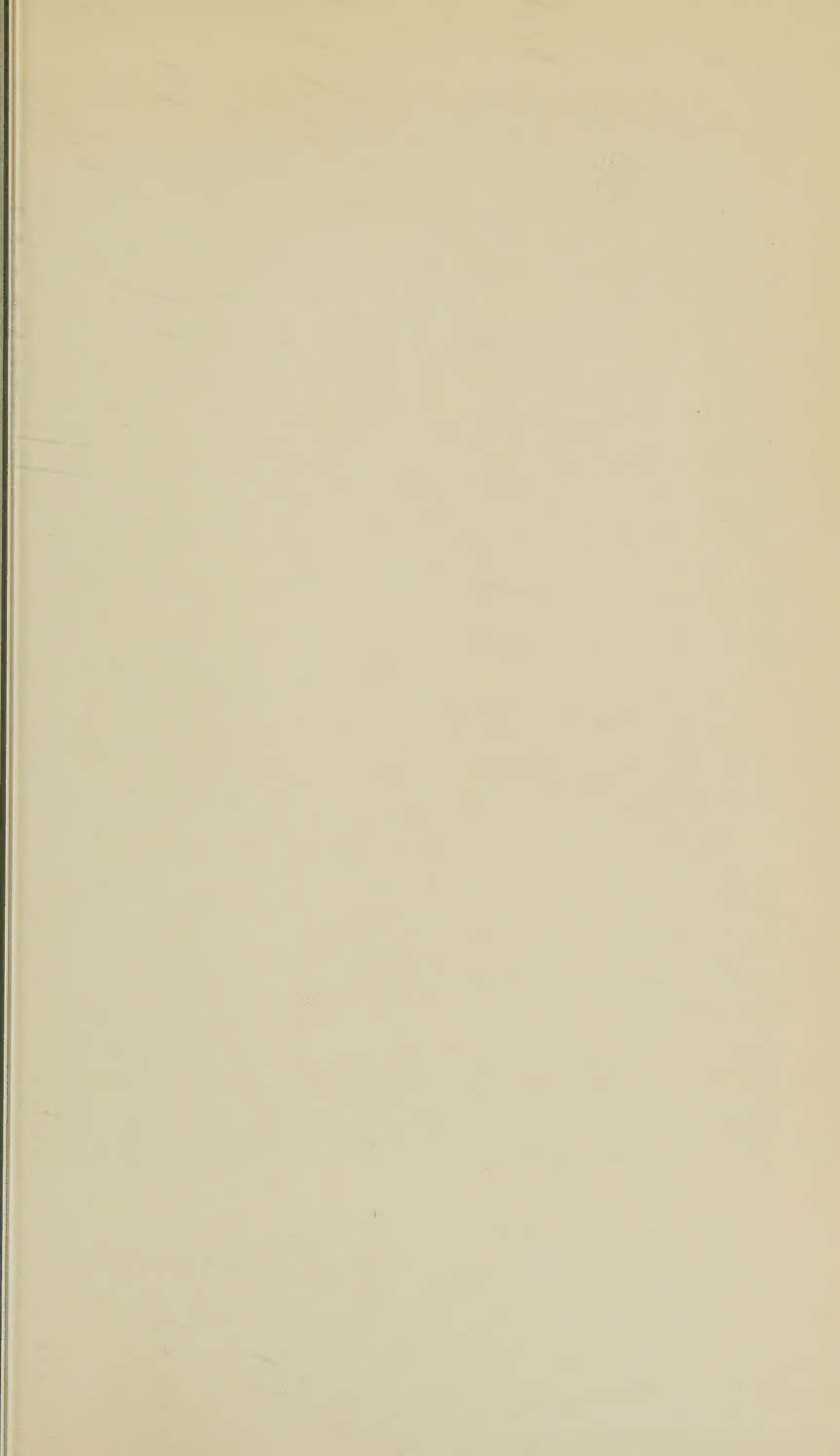
¹ M. F. Heddle, Trans. Roy. Soc. Edinburgh, 1878, vol. 28, pp. 299-319. The mineralogy of Scotland, Edinburgh, 1901, vol. 2, p. 48. [Min. Mag. 2-230, 13 194.]

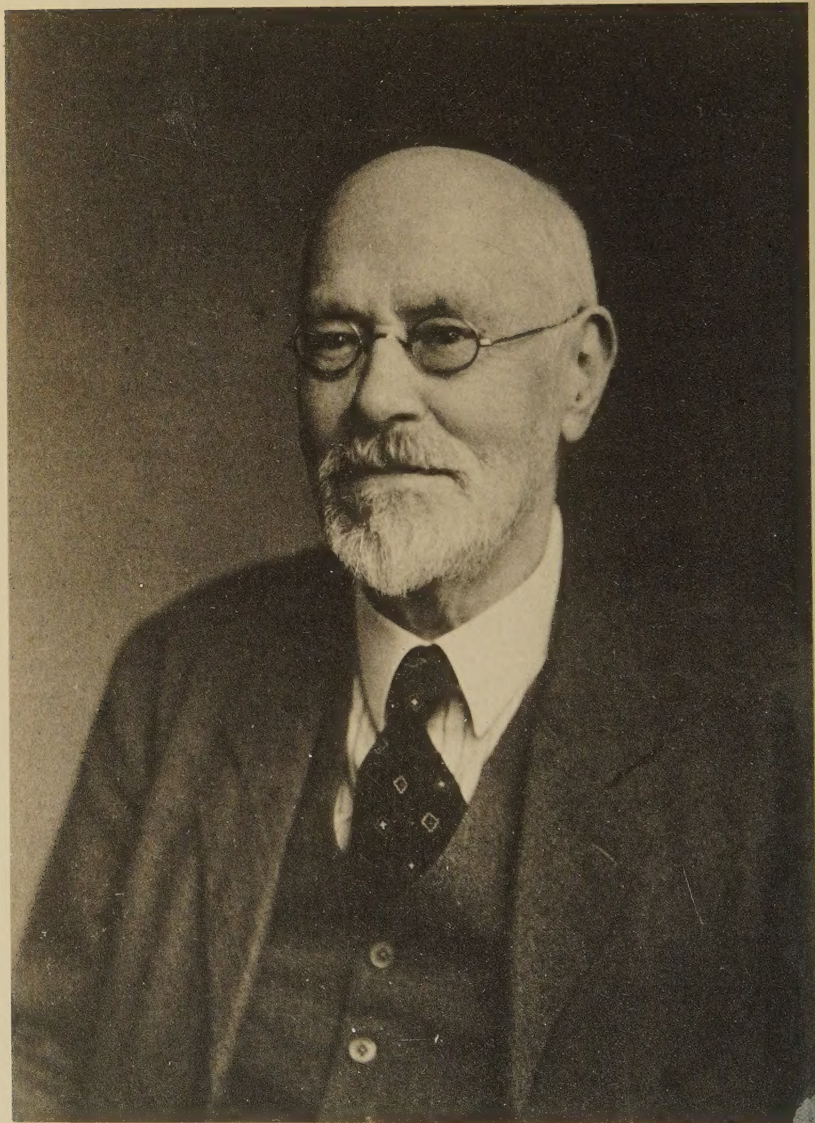
	Weight %.	Molecular ratios.		No. of metal atoms to 12 oxygens.
Si	36.59	0.6092	Si	2.888
Ti	1.68	0.0210	Ti	0.099
Al	22.42	0.2199	Al	2.084
Fe'''	0.04	0.0003	Fe'''	0.003
Fe''	32.11	0.4470	Fe''	2.119
Mn	1.42	0.0200	Mn	0.095
Mg	5.41	0.1342	Mg	0.636
Ca	0.54	0.0096	Ca	0.046
O	100.21		O	12.000

sp. gr. 4.09, n 1.804 $\pm$ 0.002. Almandine 76.47, pyrope 18.58, spessartine 3.42, molecular 1.35, andradite 0.18.

The crystals are usually covered with a thin sheath of chlorite, and are sometimes crowded with inclusions of quartz, felspar, and magnetite, which show no definite arrangement. They generally show a conspicuous parting, along which films of chlorite are often developed, and they break along this parting with curved and somewhat irregular surfaces. The parting does not appear to be parallel to any constant crystallographic direction, but rather to be related to some structural direction in the rock. In groups of crystals embedded in different orientations in the rock, the partings are approximately parallel to each other. Harker¹ has commented on similar partings in garnets of regionally metamorphosed rocks, and states that they are developed at right angles to the direction of maximum relative tension. At Cairnie they cut the planes of schistosity and gneissic banding at fairly low angles (about 15–30°). The sheaths of chlorite surrounding the crystals and the films of chlorite along the parting planes were probably formed by retrograde changes during the decline of the regional metamorphism of these rocks. The garnet partings were presumably formed before the chlorite or at about the same time, when the temperature had become sufficiently low to prevent their healing by recrystallization. One would expect the parting planes to cut the plane of schistosity at angles of 45° or greater, if the direction of maximum pressure were normal to the schistosity. As in this case they cut the planes of schistosity at low angles, it is possible that they are due to renewal of stresses at a relatively low temperature, in rather different directions to the stresses responsible for the main regional metamorphism. The fissuring of the garnets might bear a definite relationship to the new directions of stress, while the matrix might yield by rearrangement along its original planes of schistosity and not show any obvious effects of the change in stress directions.

¹ A. Harker, *Metamorphism*, London, 1939, pp. 356, 195.





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